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Preparation of hydroxyapatite-granule-implanted superplastic titanium-alloy

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In order to obtain a biomaterial that has both biological affinity and high mechanical strength, hydroxyapatite (HAp) granules were implanted into the surface of superplastic titanium-alloy. HAp granules (32–38 μm diameter) were spread over a superplastic titanium-alloy substrate and pressed to implant the granules into the substrate. This was achieved at 17 MPa, 750 °C for 10 min. Only the tops of the granules, which were surrounded by the alloy, remained exposed and they were firmly stuck in the substrate. The granules were enclosed in titanium-alloy and a reaction layer was formed at their interface. The HAp-implanted titanium-alloy composites are expected to be useful as biomaterials, such as artificial bones and dental roots. © *1998 Chapman & Hall*

1. Introduction

Owing to its biological affinity, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is a suitable material for use as biological hard tissues. However, because of its poor mechanical properties, particularly low fracture toughness, it cannot be used under a heavy load and its application is limited [1, 2]. If HAp could be coated on to a metallic material, such a composite may be a good biomaterial in terms of its affinity for a living body and high mechanical strength.

To obtain biomaterials which have both biological affinity and high mechanical strength, attempts have been made to produce a composite by coating metal with biocompatible ceramics such as HAp. With respect to the production of HAp/Ti composites, several studies and reports on composites produced by the plasma splay method, etc., have been published [3, 4]. However, it has been reported that HAp was easily decomposed by high temperature, and that HAp peels off after long-term use in a body.

A method has also been reported for the formation of TiO_2 containing calcium oxide and a complex oxide of calcium and titanium by the implantation of calcium ions into the surface of titanium. However, the thickness of the oxide film was only approximately 40 nm [5].

It is known that superplastic titanium-alloy (Ti–4.5Al–3V–2Fe–2Mo) becomes a plastic fluid when heated to approximately 750–800 °C, and it is readily formed under a pressure of 17 MPa or less [6, 7]. In this study to obtain a biomaterial which has both biological affinity and high mechanical strength, HAp granules were implanted into the surface of superplastic titanium-alloy. The HAp granules were spread over a superplastic titanium-alloy substrate and pressed with a plunger to implant them into the substrate.

2. Experimental procedure

2.1. Specimen preparation

Titanium alloy, which is Ti–4.5Al–3V–2Fe–2Mo composition (NKK, SP-700, titanium-alloy) of size 0.49 mm × 15 mm × 15 mm, was used for substrate. This alloy exhibited superplastic elongation (2000%) at 750–800 °C, so the press-forming tests were performed at 750 °C.

HAp powder was granulated using a spray-drier (STK). The granules were heated for 3 h at 1100 or 1200 °C, and then were sifted to 32–38 μm. The specimens were manufactured so that the titanium-alloy was coated with silicone grease (Coaning) and the granules adhered to its surface.

2.2. Implantation method

By using a hot press, HAp granules were implanted into the titanium-alloy substrate as follows: specimens were placed between two alumina discs, set in the hot press, and pressed under a pressure of 0.38–17 MPa for 10–180 min, at 750 °C under 0.13 Pa atmosphere.

2.3. Evaluation of properties

Specimens were removed from the hot press, and the state of reaction on their surface was checked by eye. The surfaces of the specimens were observed under an optical microscope and a scanning electron microscope (SEM).

The implantation ratio of granules was measured as follows. The diameter of the granules, (*b*), was measured using an optical microscope. The height of the projecting part of the granules, (*a*), was measured using surface analyser. The implantation ratio (%) of the granules was calculated from the

following equation

$$\text{implantation ratio}(\%) = (b - a)/b \times 100 \qquad (1)$$

To obtain an average of data points, 30 granules were measured. The composites produced were sectioned and observed under SEM. The interfaces between granules and titanium-alloy were analysed using an electron probe microanalyser (EPMA).

3. Results and discussion

3.1. Properties of HAp granules

Granules are porous, having a specific pore size of approximately 1 μm. Judging from the XRD patterns, the precipitation phase is HAp.

3.2. Implantation

Granules were not deformed at a uniform implantation of every specimen. The joint area of the substrate adhered closely to the granules, and the surface of the titanium alloy showed a metallic gloss. No change was observed.

Figs. 1 and 2 show scanning electron micrographs of the specimens which were pressed under 0.38 MPa at 750 °C. For implantion times of 10 min, the implantation ratio was approximately 20% and some granules were not on the substrate. After 60 min implantation, the implantation ratio was 100%, but the upper areas of granules were exposed. The titanium alloy near the granules was deformed by the implantation, and deep hollows were seen.

Fig. 3 shows scanning electron micrographs for the specimens which were pressed under 0.75 MPa at 750 °C for 10 min. The implantation ratio was 50%.

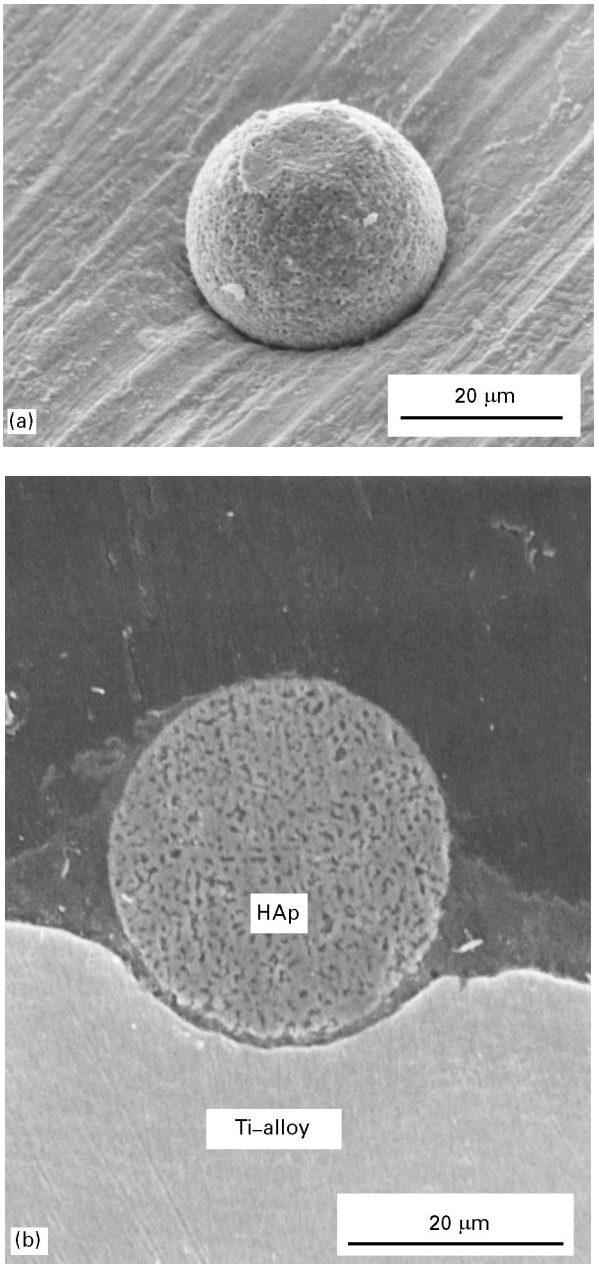

Figure 1 Scanning electron micrographs of specimens with HAp granules implanted into titanium alloy at 750 °C for 10 min at 0.38 MPa: (a) surface, (b) cross-section.

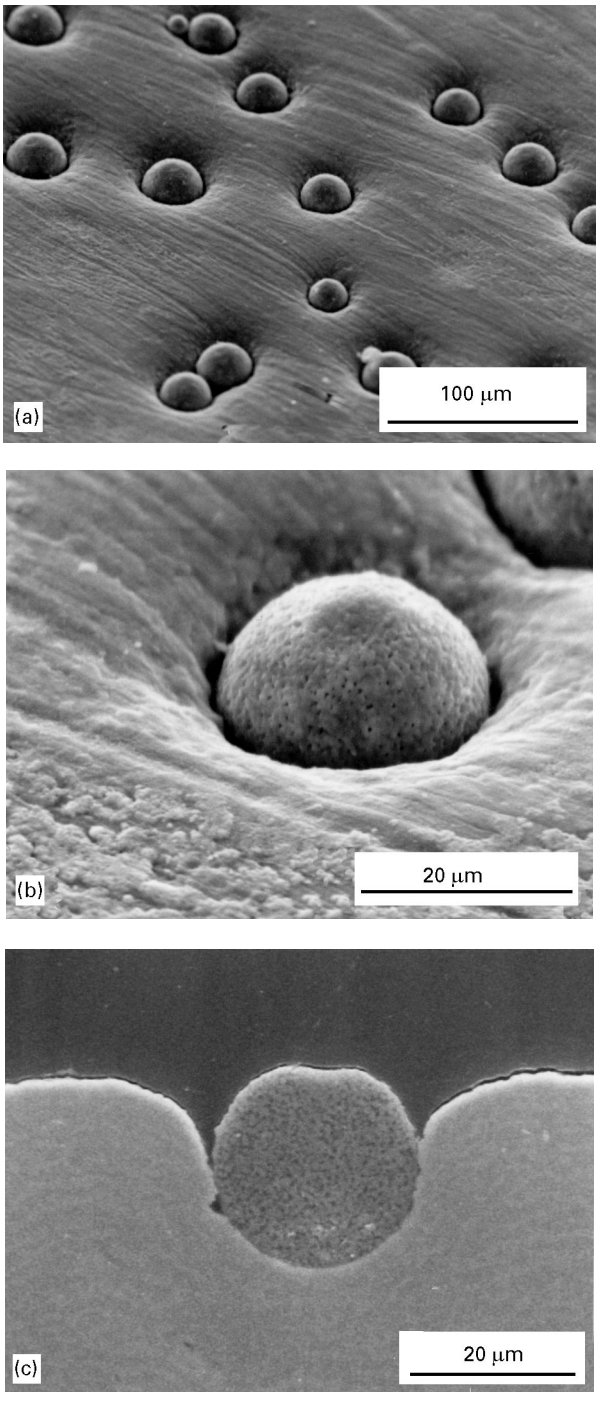

Figure 2 Scanning electron micrographs of specimens with HAp granules implanted into titanium alloy at 750 °C for 60 min at 0.38 MPa: (a, b) surface, (c) cross-section.

The titanium alloy near the granules was deeply hollowed and the upper part of the granules was exposed.

Figs. 4–6 show scanning electron micrographs for the specimens which were pressed under 8.5 and 17 MPa at 750 °C. The implantation ratio was 100%.

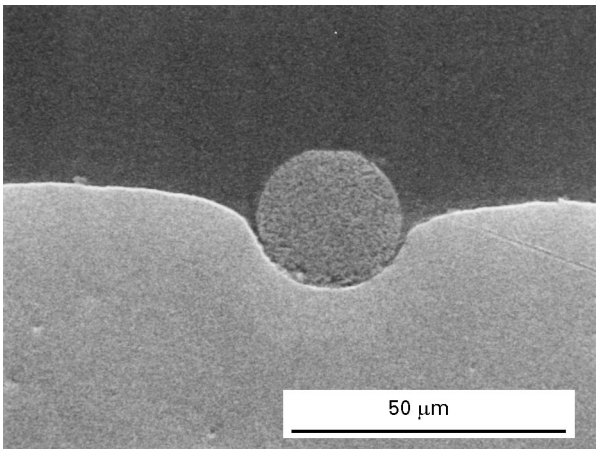

Figure 3 Scanning electron micrograph of specimen with HAp granules implanted into titanium alloy at 750 °C for 10 min at 0.75 MPa (cross-section).

The substrate which was directly in contact with the alumina plunger is clearly evident. Only the topmost part of the granules was exposed, the remainder being surrounded by titanium alloy, and firmly stuck in the substrate. With increasing implantation pressure, the contact area between granules and substrate spread. Scanning electron micrographs indicated that the hollowing of the substrate around the granules was smaller than for the specimen implanted under a pressure of 0.38 MPa.

Under a pressure of 0.38 MPa, the longer the implantation time, the deeper were the granules buried, but the upper part of the granule was not covered with alloy because of the small stress. On the contrary, under a pressure of 17 MPa, the upper part of the granules was covered with alloy and they adhered to the substrate.

These facts clarify that the implantation process of a granule is divided into the following two steps.

1. First, the granules are implanted to a depth which corresponds to the diameter, with a small stress.

2. Secondly, the complete specimen is produced as the titanium alloy moves over the upper part of the granules which are then firmly stuck in the substrate.

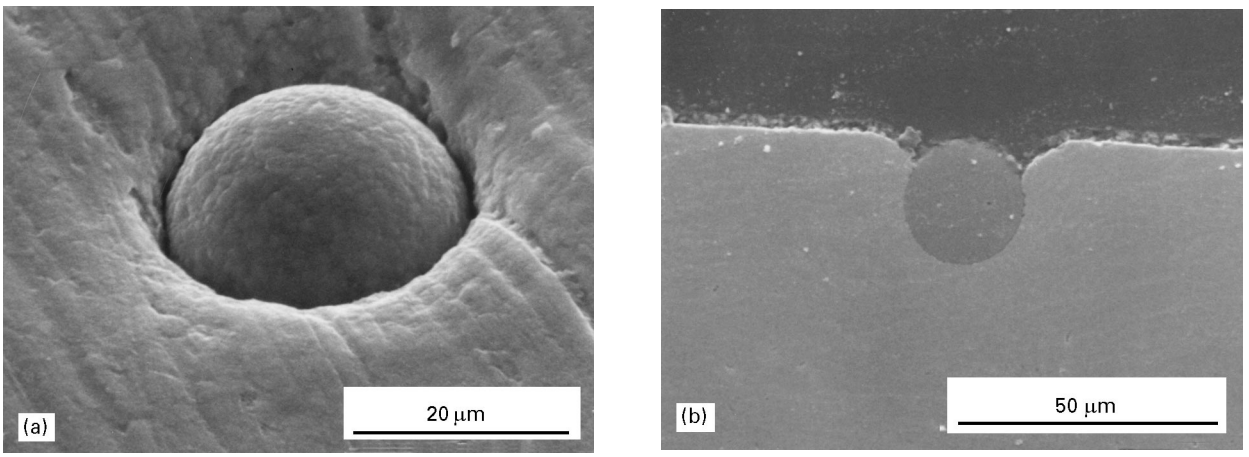

Figure 4 Scanning electron micrographs of specimens with HAp granules implanted into titanium alloy at 750 °C for 10 min at 8.5 MPa: (a) surface, (b) cross-section.

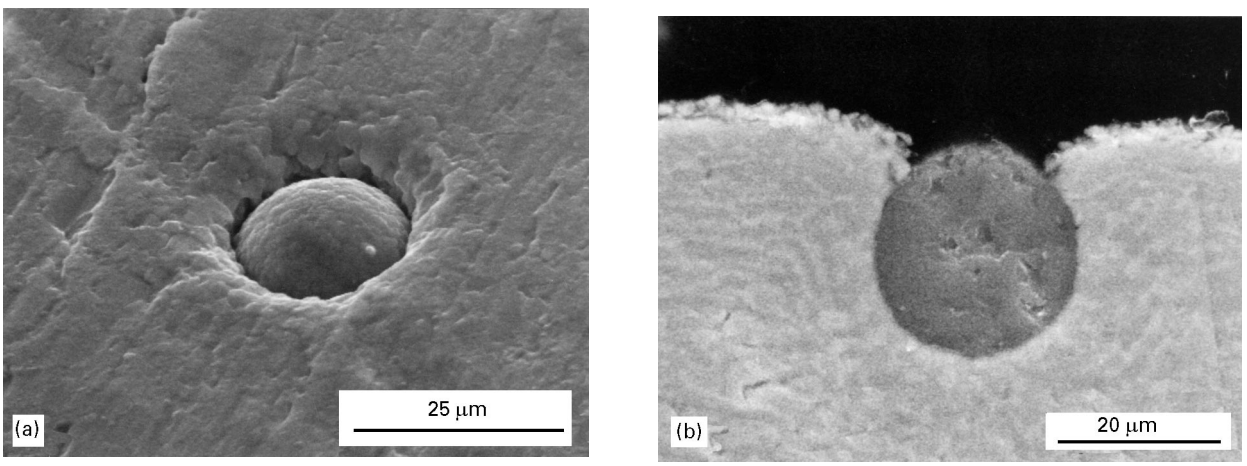

Figure 5 Scanning electron micrographs of specimens with HAp granules implanted into titanium alloy at 750 °C for 60 min at 8.5 MPa: (a) surface, (b) cross-section.

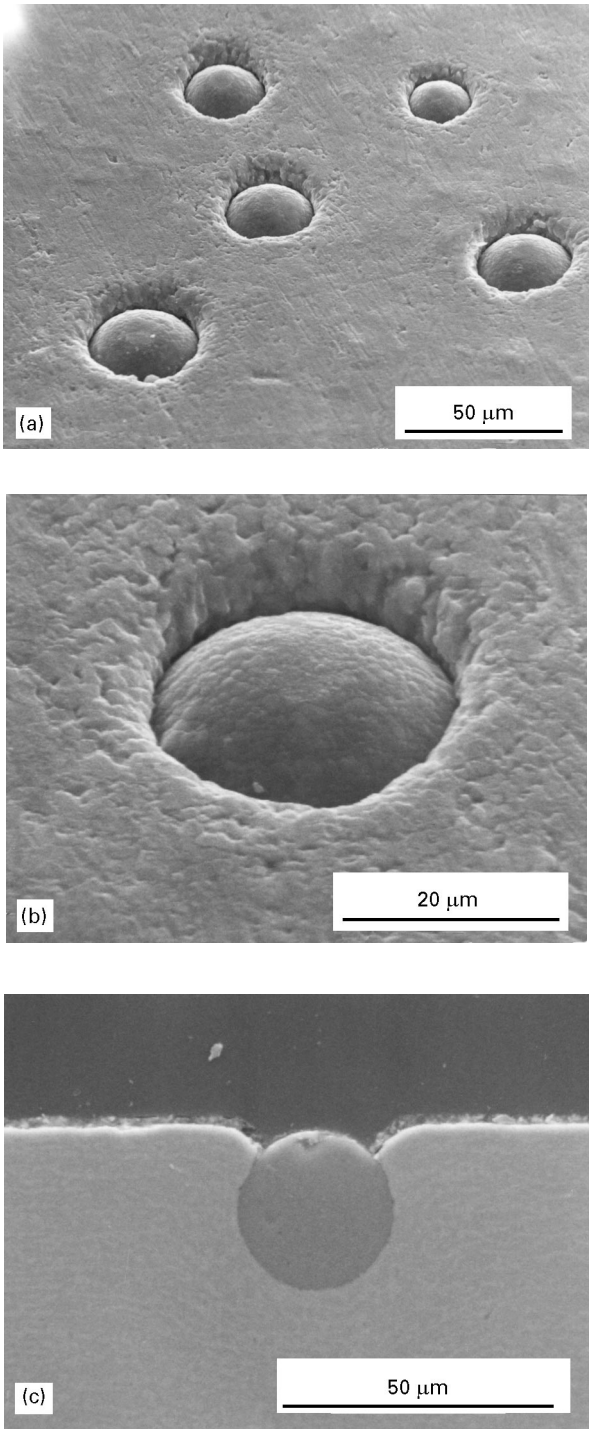

Figure 6 Scanning electron micrographs of specimens with HAp granules implanted into titanium alloy at 750 °C for 10 min at 17 MPa: (a, b) surface, (b) cross-section.

3.3. Interface between HAp and titanium alloy

An EPMA spectral diagram showing the change of composition across the interface of the HAp granule with the titanium alloy is shown in Fig. 7. Titanium, aluminium and iron diffused to the granule. Calcium, oxygen and phosphorous diffused to the titanium alloy. Silicon is present in the interface. The thickness of the interface was about 1 μm. Silicon, which was included in the silicone grease, was diffused and SiO_2 was probably formed. Thus the granules are chemically combined to the alloy.

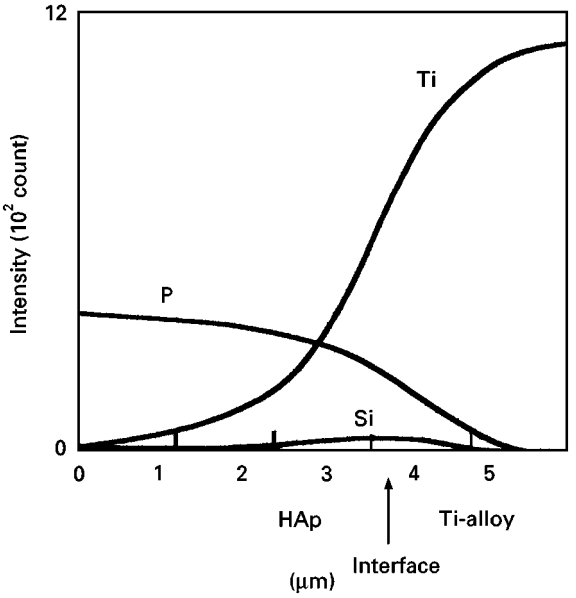

Figure 7 EPMA line profiles of the interface between the HAp granule and the titanium alloy.

4. Conclusions

To obtain biomaterial that has both biological affinity and high mechanical strength, HAp granules were implanted into the surface of superplastic titanium alloy. The HAp granules (32–38 μm diameter) were spread over a superplastic titanium alloy substrate and pressed to implant them into the substrate.

1. Granules were implanted at 750 °C, 0.38 MPa for 1 h; the implantation ratio was 100%, but the upper part of the granules was exposed. The titanium alloy near the granules was deformed by implantation and had deep hollows.

2. Under a pressure of 17 MPa, the implantation ratio was 100%. The only part of the granules not surrounded by titanium alloy was the top, and the granules were firmly stuck in the substrate.

3. The granules were enclosed in the titanium alloy and a reaction layer formed at the interface between them.

The HAp-implanted titanium alloy composites are expected to find use for biomaterials such as artificial bones and dental roots.

References

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