Preparation of hydroxyapatite-granule-implanted titanium alloy composites with a cylindrical shape

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For uniformly implanting hydroxyapatite (HA) granules into curved surfaces of titanium alloy implants such as dental roots, a new superplastic forming system was developed. By fixing PVA films with HA granules on a die's curved inner surface, HA granules are uniformly scattered and hold on the surface. The pressing system has a couple of wedges that enable press load to act on the both sides of a cylindrical titanium alloy sample arranged with its long axis perpendicular to the direction of the load in the die, and thereby the sample to expand in its radius direction. This technique could uniformly press HA granules into all the curved surface of titanium alloy. As a result, HA-granule-implanted titanium alloy composites with a cylindrical shape were formed under the conditions of 1023 K, 1 h, 1960 N in vacuo.

1. Introduction
Titanium alloys are useful for biological application such as dental and surgical implants, because they are fixed within a bone bed through direct attachment to bone (osseointegration) [1]. However, bone-bonding strength of titanium alloys is weaker than that of bioceramics such as hydroxyapatite (HA) [2]. Bioceramic coating on a titanium alloy has been intensively studied in order to obtain implant materials which have both biological affinity and high mechanical strengths [2–4]. Plasma spraying, etc. are the methods developed recently to achieve HA coating [5] on titanium alloy implants. HA plasma-spraying is performed at an elevated temperature almost 10 000 K [6–8], thence various problems occur in the composition, crystallinity and structure of the coated HA layer and degradation of the HA layer is inevitable due to thermal unstablity [9].

In our previous study, we have developed a method for obtaining a bioactive surface of superplastic titanium alloy (Ti-4.5Al-3V-2Fe-2Mo), that is HA-granule-implantation into titanium alloy flat surface [10]. It is known that the superplastic titanium alloy shows the superplasticity when heated to approximately 1023–1123 K, and it is readily formed under a pressure of about 17 MPa [11, 12]. By this method, HA granules, which were fixed on the plates by silicone grease (Coaning) in advance, were pressed into a titanium alloy flat surface at 1023 K and they were pushed into the surface by the plastic deformation of titanium alloy. When the deformation of the titanium alloy plate is controled properly, the HA granules were held mechanically in the surface with their topmost parts exposed outside. However, by this process, uniformly scattering and fixing HA granules into curved surfaces are difficult. Thence, for applying this method to practical implants such as dental roots, it is necessary to develop another process implanting HA granules onto the curved surface of titanium alloy.

In this paper, we report a new designed superplastic forming system [13, 14] for getting the titanium cylinders that have a HA-granule-implanted surface. By the system, not only titanium cylinder surfaces are modified with the HA-granule-implantation, but also the titanium cylinders can be formed into the last product shape.

2. Experiment
Ti-4.5Al-3V-2Fe-2Mo superplastic alloy (SP-700, NKK Co.) was used for this study. This material's samples with cylindrical shape (2.8 mm diameter, 11.5 mm length) were prepared by lathing.

HA powder (STK Ceramics Co.) was heated at 1373 K for 3 h in the air in order to be stiffened, then sifted to get the granules that were within 38 μm diameter. The HA granules were dispersed with 3.8 wt % polyvinyl alcohol (PVA, Wako Pure Chemical Industries, Ltd.) aqueous solution (mw = 2000) with the concentration of 0.1 g HA granules/1 g solution. This solution was dried up in an area 25 cm^2 on a horizontal glass surface, and the resulted PVA film contained HA granules as 4 mg/cm^2. This film was fixed on the inner surface of ceramic cylindrical dies (H type machinable ceramics: AlN/BN

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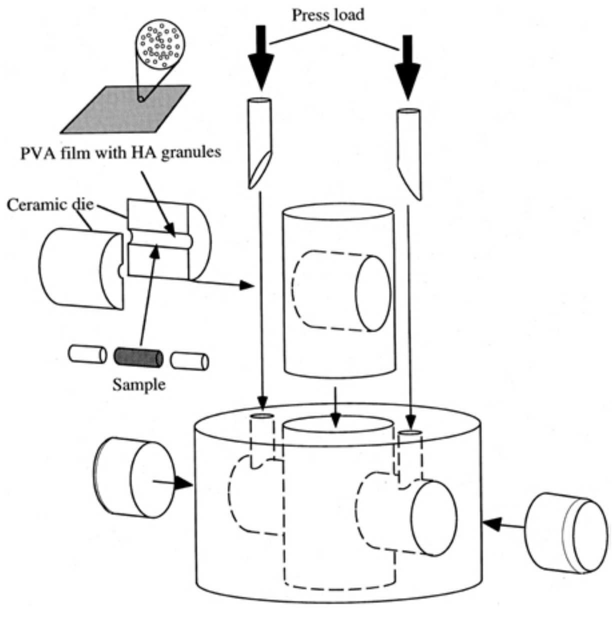

Figure 1 Schematic diagram of die and pressing system for forming HA-granule-implanted titanium alloy composites.

composite, inner diameter: 3.0 mm, Ishihara Chemical Co.). As a result, the die possessed HA granules on its inner surface.

Fig. 1 shows a schematic diagram of a die and a plastic forming system. A cylindrical sample was set into the die that was mounted in the system, and the long axis of the sample was kept in horizontal direction. Then the mold was placed into a hot-press furnace. After the hot-press chamber was evacuated to 0.01 Pa, the system with the cylinder sample was heated up at 1023 K, and press load (1960 N) was added with a press rod's speed of 0.05 mm/min in 10 min, 30 min or 1 h. The system has a couple of wedges which enable the pressure compressing to the sample horizontally from both sides. The sample theoretically takes the pressure of about 140 MPa. As a result, the sample expanded radially with shrinking in the long axis and the HA granules were pressed into the surface of the sample. Specimens were removed from the die after the deforming process, and the state of their surface was checked by eye. The obtained samples were sectioned in round at center, and then the sample observed by a scanning electron microscope (SEM). The interfaces between granules and titanium alloy were analyzed by an electron probe microanalyzer (EPMA). The depth profile of elemental signals of boron, carbon, oxygen and titanium around the titanium alloy surface were analyzed by an auger electron spectroscopy (AES) with using the Ar ion etching device.

3. Results and discussion

3.1. Implantation of the HA granules onto titanium alloy cylinders

The surfaces of obtained samples keep its metallic color. Fig. 2 indicates the surface SEM photographs of typical surfaces and cross sections of the samples. By the deforming processes of 10 min and 30 min pressing time, the HA granules were not fully pushed into the surface of the cylinder, and the HA granules projected over titanium alloy surface. In this case, several HA granules were broken and degraded, and the ratio of broken HA granules on the samples deformed in 10 min was much than that of the samples deformed in 30 min. On the other hand, HA granules on the surface of sample deformed in 1 h were fully implanted into titanium alloy and the granules have no crack. This means that the former samples were damaged when removed from the die. In other words, the HA granules, which were not fully implanted into titanium alloy, were easy to take high stress from the die, then the several granules were broken. On the sample implanted HA granules fully, titanium alloy surface area was clearly observed, only topmost part of the granules was exposed, and bottom of the granules was closely surrounded by titanium alloy. The granules were not deformed and the interface between the granules and titanium alloy adhered closely. Thus HA granules were held mechanically by titanium alloy. The sample was with 3 mm diameter and 10 mm length.

3.2. Analysis of HA/titanium alloy interface and sample's surface

Fig. 3 shows the elemental signals of calcium, phosphorus, oxygen and titanium around the interface between HA granule and titanium alloy by an EPMA. The elemental signals of calcium, phosphorus and oxygen were observed from the interface to about 1 μm depth in titanium alloy and its distance was as same as the measurement error of EPMA. Therefore, even if there is diffusion, its quantity is small, and diffusion distance is within 1 μm.

Fig. 4 indicates that the AES in-depth profiles of carbon, boron, oxygen and titanium at the surface of titanium alloy deformed in 1 h. The elemental signals of carbon and boron were observed from the surface to the depth of about 1 μm or lower, thence contaminated layer was at least within 1 μm. The thickness of titanium oxide layer was less than 0.5 μm. Because of the processes in the vacuum atmosphere, the thickness of the oxide layer might be restrained.

4. Conclusions

HA-granule-implanted titanium alloy composites with a cylindrical shape were obtained by using a new process. Superplastic titanium alloy (Ti-4.5Al-3V-2Fe-2Mo) cylindrical samples were superplastically deformed at 1023 K in 1 h and the samples expanded in the radius direction with shrinking in long axis in a die which had PVA film with HA granules on those inner surface. As a result, the samples with 2.8 mm diameter and 10 mm length were shaped to 3 mm diameter and 10 mm length. At the same time, the surface of the sample was modified with the HA-granule-implantation. Contaminated layer in the sample was less than 1 μm. By this technique, preparation of HA-granule-implanted titanium alloy implants with other shapes is also possible.

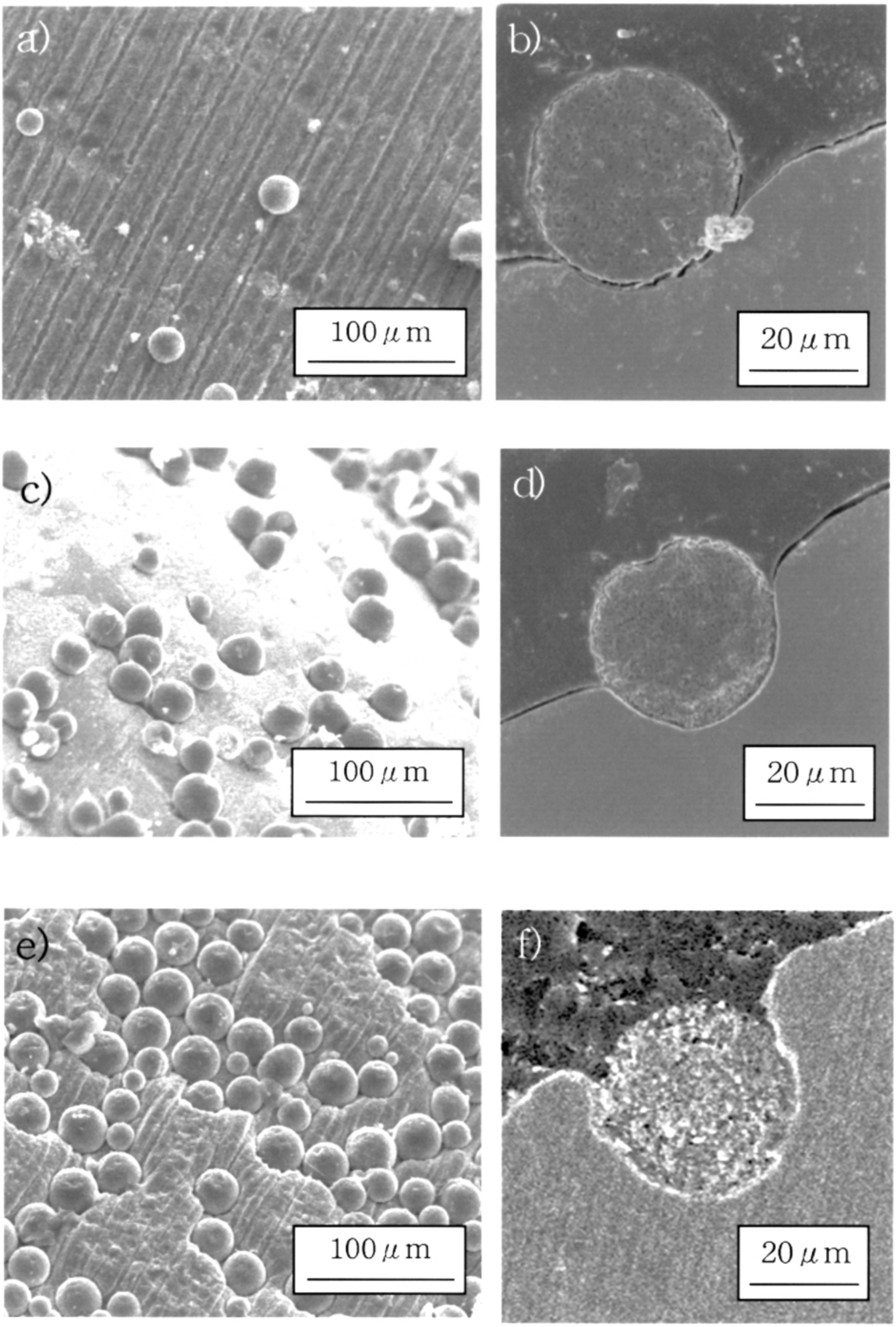

Figure 2 SEM photographs of surfaces and cross sections of the samples deformed at 1023 K, 1960 N in (a,b) 10 min, (c,d) 30 min, (e,f) 1 h.

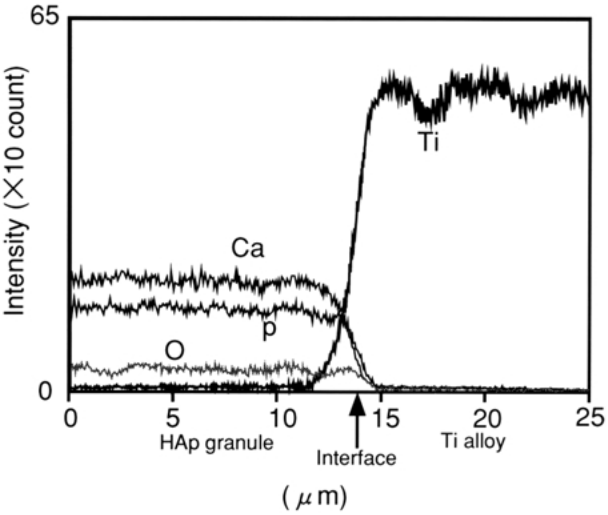

Figure 3 The EPMA elemental signals of calcium, phosphorus, oxygen and titanium around the interface between HA granule and titanium.

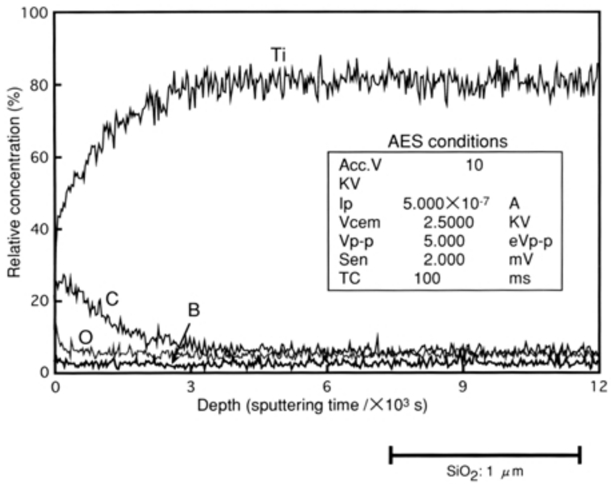

Figure 4 The AES in-depth profiles of carbon, boron, oxygen and titanium at the surface of titanium alloy deformed at 1023 K, 1960 N, 1 h.

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