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Characterization of the hydroxyapatite layer formed by fine hydroxyapatite particle peening and its effect on the fatigue properties of commercially pure titanium under four-point bending

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ABSTRACT

Fine particle peening (FPP) using hydroxyapatite (HAp) shot particles was introduced to form the HAp surface layer and improve the fatigue properties of commercially pure (CP) titanium. The surface microstructure of the FPP-treated specimens was characterized using a micro-Vickers hardness tester, optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD), and non-contact scanning white light interferometry. FPP could create a HAp layer on the surface of CP titanium within a relatively short time (1 s) by shot particle transfer. In addition, FPP increased the surface hardness and generated compressive residual stress at the treated surface. Four-point bending fatigue tests were performed at a stress ratio of 0.1 in air at room temperature to examine the effect of FPP using HAp shot particles on the fatigue properties of CP titanium. It was found that the fatigue limit for the FPP-treated specimen was higher than that for the unpeened specimen. The fatigue fracture mechanism for the CP titanium treated with FPP was discussed from the viewpoint of fractography. The HAp layer remained on the surface without delamination after the fatigue tests.

1. Introduction

Commercially pure (CP) titanium and titanium alloys are widely used in various fields of engineering. In particular, CP titanium is applied to biomaterials due to its excellent corrosion resistance, high tissue compatibility, and absence of physically harmful elements. Moreover, CP titanium has a low Young's modulus in comparison with ferrous materials; therefore, this material is often used as a substitute material for biological hard tissues to prevent stress shielding, such as in artificial joints, dental implants, and fracture fixators.

For titanium-based bio-implants, osteoconductivity (the characteristics related to bone growth on a material's surface) is needed because an extended period of time is required to fix them with human bones. In order to improve the osteoconductivity and bonding strength between human bones and bio-implants, various surface treatments have been proposed [1–11]. Mainly, two methods are effective for improving the hard tissue compatibility of titanium-based bio-implants: surface modification to create a bioactive material surface and coating with hydroxyapatite (HAp). For example, Sugino et al. [1] investigated the effects of thermal oxidation on HAp formation in Ti–15Zr–4Ta–4Nb alloy and the possibility of promoting osteoconductivity. In contrast, Kuriyagawa et al. [5,6] proposed that a HAp film can be formed on a human enamel substrate using powder jet deposition for dental therapy, and Inagaki et al. [7] reported that partial nitriding improved the bonding strength of plasma-sprayed HAp/titanium composite coatings on titanium.

Furthermore, fatigue strength is also needed for titanium-based bio-implants because of the cyclic loading applied to them while implanted in the human body. Apachitei et al. [11] examined the effect of shot peening prior to plasma electrolytic oxidation coating on the fatigue strength of Ti–6Al–4V alloy. However, the strength of CP titanium is generally lower than that of titanium alloys such as Ti–6Al–4V and, therefore, should be improved. Based on these considerations, fine particle peening (FPP) using HAp shot particles was introduced to form the HAp surface layer and improve the fatigue properties of CP titanium. In our previous studies [12–15], we focused on shot particle transfer by FPP and proposed it as a new surface modification method. Kameyama et al. [15–17] clarified that transferred fragments were brought onto the substrate surface, and a surface-modified layer was

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Table 1
Chemical composition of CP titanium (mass%).

C	O	N	Fe	Ti
0.01	0.10	0.004	0.02	Bal.

then formed due to repeated covering during FPP. Moreover, compared with conventional shot peening, FPP is more effective for generating high and stable compressive residual stress [18] and creates fine crystal grains [19–22], which results in improved fatigue strength. This is because the particle velocity in FPP is higher than that in conventional shot peening [23–26]. Therefore, it is expected that FPP using HAp shot particles will improve the fatigue strength of CP titanium and form the HAp surface layer.

The purpose of this study was to characterize the HAp layer formed on CP titanium by FPP using HAp shot particles. Furthermore, the fatigue properties of CP titanium treated with FPP using HAp shot particles were experimentally examined by performing fatigue tests under four-point bending.

2. Experimental procedures

2.1. Material and specimen preparation

CP titanium (Grade 2) with the chemical composition shown in Table 1 was used in this work. Fig. 1 shows an optical micrograph of the as-received material with a 47 μm average grain size. This material has a Vickers hardness of 288 HV, which was measured on its polished surface with an indentation force of 0.098 N and a load holding time of 10 s ($n = 30$). CP titanium plates 13 mm in thickness were machined into sheets 1.5 mm in thickness and then into specimens 3 mm in width and 20 mm in length using a wire electrical discharge machine. After machining, these specimens were polished with emery paper (#320 to #4000) to 1 mm in thickness with a mirror finish using SiO_2 suspension. The sides of the specimen were also polished with emery paper (#500) to remove the electro-discharge machined layer.

FPP was performed on the polished specimens using a direct pressure type apparatus under the conditions given in Table 2 at room temperature in air. The shot particles used in this study were produced by braying HAp of 38.7 HV with 10–15 mm diameter using an earthenware mortar and were 50 μm in average diameter. Fig. 2 shows a scanning electron microscopy (SEM) micrograph of HAp shot particles with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$. After performing FPP, some specimens were placed inside an ultrasonic acetone bath for 600 s to remove the free particles on the specimen.

Table 2
Peening conditions.

Treatment apparatus	Direct pressure type
Shot particles	Hydroxyapatite
Peening pressure, MPa	0.6
Peening time, s	1, 10, 20, 30
Nozzle distance, mm	50

2.2. Characterization of the surface-modified layer

The hardness distribution was measured along the cross section of the FPP-treated specimen embedded in epoxy resin using a micro-Vickers hardness tester with an indentation force of 0.49 N and a load holding time of 10 s. The surface microstructure of the specimens was characterized using optical microscopy and SEM. The surface morphology of the specimens was analyzed using non-contact scanning white light interferometry, and the average value of the arithmetic mean deviation *Ra* was calculated ($n = 10$). The FPP-treated surface was analyzed by energy dispersive X-ray spectrometry (EDX) for an area (1.13 mm^2) observed at 100× magnification at an accelerating voltage of 20 kV. The crystal structure of the specimens was identified using X-ray diffraction (XRD) with CuKα radiation. The residual stress was also measured at the top surface and at given depths for the transverse section of the specimen by XRD with CoKα radiation with a position-sensitive proportional counter (PSPC) system based on the $\sin^2\psi$ method ($n = 2$) [27, 28]. The conditions for the residual stress measurement are shown in Table 3.

2.3. Fatigue tests under four-point bending

Fatigue tests were performed under four-point bending in air without any temperature or moisture control at a stress ratio of $R = 0.1$ and a frequency of 10 Hz. In this study, the fatigue limit was defined as the average of the maximum stress amplitude without specimen failure and the minimum stress amplitude at which the specimens fail. After testing, the fracture surfaces of the failed specimens were observed by SEM at an accelerating voltage of 10 kV.

3. Results and discussion

3.1. Characterization of HAp layer formed by FPP on CP titanium

Fig. 3 shows optical micrographs of the surfaces treated with FPP for 20 s (a) without cleaning and (b) with cleaning using acetone. For the area indicated by an arrow in this figure, FPP was not performed. It

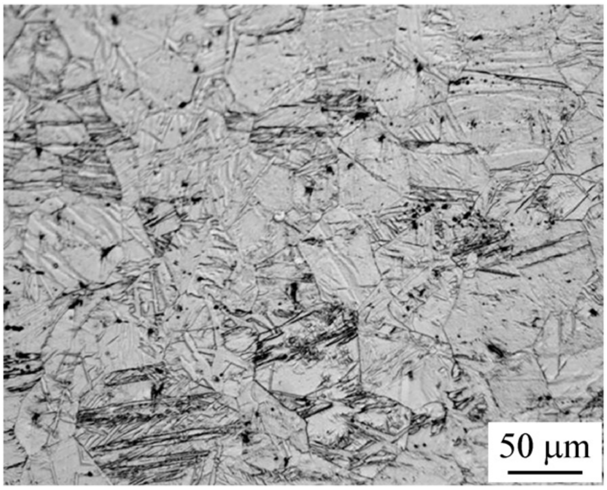

Fig. 1. Optical micrograph of as-received CP titanium.

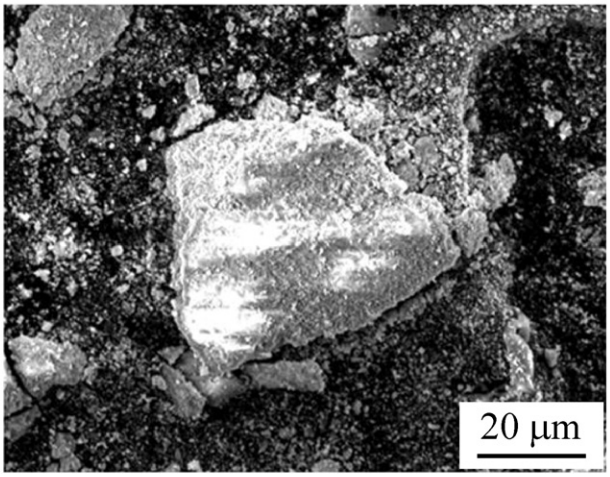

Fig. 2. SEM micrograph of hydroxyapatite (HAp) shot particles.