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Mechanical and biological stability of superplastically embedded HA nanolayer deformed at high temperature

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ABSTRACT

In this study, HA is superplastically embedded into Titanium substrate and the sample is subsequently deformed superplastically until 70% deformation degree. The former process is termed as superplastic embedment (SPE) while the later as superplastic deformation (SPD). After the SPE, HA is successfully embedded into the substrate, forming a layer with a thickness of about 249 nm. After the SPD the embedded HA layer thickness decreases to 111 nm. The SPD sample is then immersed in simulated body fluid (SBF) to evaluate its biological properties. A newly grown apatite is formed as a result of the immersion and the HA layer thickness increases with immersion time. The cohesion and adhesion strength within the HA coating and coating-substrate interface of the SPD samples before and after immersion in the SBF is evaluated through the nanoscratch test technique. The results indicate that the HA layer after SPD is still strong even though after being exposed in SBF environment for quite some time. The study suggests that the superplastically embedded HA nanolayer is still intact mechanically and functioning appropriately as biological activity base even after the SPD process.

1. Introduction

Titanium and titanium alloys are widely used for implant materials due to their combination of most favourable characteristics including immunity to corrosion, bio-compatibility, strength and low modulus and density [1]. Unfortunately, due to the lack of a specific biological response from the living tissues, the titanium implant can progressively form a non-adherent fibrous capsule around the implant, leading, in some cases, to interfacial displacements and clinical failures [2,3]. Moreover, a certain degree of chemical degradation of these metals may occur [2,4].

Hydroxyapatite (HA) is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of few materials that are classed as bioactive, which means it will support bone ingrowths and osseointegration when used in orthopedic, dental and maxillofacial applications. But, due to its poor mechanical properties (fatigue properties) hydroxyapatite cannot be used in bulk form for load bearing application such as orthopedics [5].

Coatings of hydroxyapatite onto Ti-6Al-4V have good potential as they can exploit the biocompatible and bone bonding properties of the ceramic, while utilizing the mechanical properties of substrate [6]. There are many techniques in coating of hydroxyapatite and one of the most applied techniques is thermal spraying or plasma spraying. This technique can coat complex substrates and have high deposition rates. However, it is difficult to prepare a uniform coating on a metal alloy implant with a complex structure, due to low bonding strength [7]. Besides that, the interactions between input variables make its control logic to be complex [8] and therefore making this technique more complicated.

With the aim to improve the bonding strength of the coating, an alternative coating method must be explored. Superplastic deformation method is quite interesting since its polycrystalline materials are able to exhibit very high value of strain [9,10]. Application of superplastic deformation in industrial forming of alloys offers advantages mainly related to possibility of producing elements having complex shape [11]. In medicine, superplastic deformation becomes new and interesting alternative method for forming biomaterials and producing implants [12–14]. HA layer with good bonding strength is successfully produced when HA is superplastically embedded into Ti-6Al-4V alloy [15]. Further study on this subject matter indicates that the superplastically embedded HA layer is still strongly intact to the substrate surface even after further deformed at high temperature without deteriorating the HA structure [16]. However, to form a complex structure of implant, higher deformation degree is required.

In order to achieve the aforementioned goal, this study is based from the previous works method [16], which the superplastically embedded sample is further deformed to 70% deformation degree. The HA layer properties in terms of biological and mechanical are then evaluated to conform its suitability for medical implant applications.

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2. Materials and method

Ti-6Al-4V bar shape having a dimension of 35 mm × 3 mm × 3 mm is used as the substrate material. HA powder with a mean diameter of 10 ± 0.5 μm is used as embedment material and is supplied by Taihei Chemical Co. Ltd. Tokyo, Japan. In order to obtain suitable condition of substrate during superplastic embedment process, the as-received Ti-6Al-4V is solution-treated above the β transus temperature (1373 K) for 30 min and ice-quenched to room temperature [16–18]. Prior to the embedment process, the heat treated sample surfaces are polished using emery paper with a grit size of 100 up to 1200 and cleaned with ethanol to remove oxide layers and irregularities [16].

The superplastic embedment process is carried out at temperature 1200 K under a strain rate of 1×10^{-4} s^{-1} [15] to 54 % deformation degree [16]. After the process is completed, the specimen is furnace cooled to room temperature. This process is termed as superplastic embedment (SPE). Fig. 1 shows the experimental set-up in schematic diagram.

The next process is to superplastically deformed the HA embedded sample at temperature 1200 K under a strain rate of 1.6×10^{-3} s^{-1} [16] to 70 % deformation degree. The specimen is furnace cooled to room temperature after the deformation process is finished. This process is termed as superplastic deformation (SPD). Here, the experimental set-up that is similar with the earlier superplastic embedment process except there is no HA powder is involved.

Both of the high temperature deformation processes are performed using compression testing machine (Instron) equipped with high-temperature furnace in argon gas atmosphere (controlled gas).

After the deformation process is done, the sample is carefully cleaned with distilled water and ethanol as preparation for the in-vitro analysis. In the analysis, the deformed embedded samples are immersed in 20 mL SBF (Simulated Body Fluid) and kept at 37 °C in a closed container for 1, 7 and 12 weeks. The SBF is refreshed every three days in order to maintain the ion concentration during immersion period.

The morphological and elemental analysis of the HA coating before and after immersion in SBF is carried out by Field Emission Scanning Electron Microscopy (Zeiss FESEM) equipped with energy dispersive X-ray spectrometry (EDX). The characterization of crystallographic structure of HA on the Ti substrate is measured by using X-ray diffraction (XRD, Bruker D8 Advance) and the Vickers microhardness machine is used for surface hardness measurement. The cohesion and adhesion strength of the HA layer is evaluated through nanoscratch technique (Micro Materials NanoTest (Wrexham, UK)). A conical indenter is used as a stylus. The scratches are produced by applying linearly increasing load (up to 100 mN and 500 mN) on the stylus with 1000 μm fixed scratching length.

3. Results and discussion

3.1. Heat treatment

Fig. 2a shows the image of the as-received Ti-6Al-4V microstructure. The microstructure is composed of equiaxed α grains and β phase (fine lamellar structure) in the form of thin layers separating the α grains. After the solution treatment process, alloy microstructure transforms into martensitic α′ phase. The structure of martensite α′ is indicated by the presence of thin lamellae resembling needles in Fig. 2b.

3.2. Superplastic embedment (SPE) and superplastic deformation (SPD) processes

Fig. 3 shows the stress-strain relationship for the SPE and SPD processes. A typical increase in stress with strain is observed for the two processes. The maximum stress obtained during SPE and SPD is 154 MPa and 164 MPa respectively. SPD has relatively higher stress than SPE because of its higher strain rate.

The substrate's microstructures after the SPE and SPD are shown in Fig. 4. After the SPE, the marten site α′ transforms into fine equiaxed microstructure with 2 ± 0.2 μm grain size. A slight increase in grain size is observed (3 ± 0.6 μm) after the SPD. However it is still relatively very fine and far smaller than the general size (less than 10 μm) required for any superplastic deformation to occur.

After SPE, HA is successfully embedded into the substrate - forming a layer having a thickness of about 249 nm in average - as shown in Fig. 5a. After the SPD - where the sample is further deformed to 70 % deformation degree - the embedded HA layer loses some of its thickness as shown in Fig. 5b. The HA layer thickness after SPD is approximately 111 nm in average. The HA layer loses more than half of its thickness. The surface morphologies of the embedded HA after the SPE and SPD are shown in Fig. 6a and b respectively. As compared to a rather smooth surface after SPE, after SPD the surface is relatively rough. Pores (marked by the white circles) and cracks (marked by the white arrows) are seen on the surface indicating surface deteriorations caused by the compression force during SPD. These trends are quite similar with our previous work [16] where the embedded HA layer thickness is reduced and the surface deteriorated with deformation degree. However, the positive side here is that there is still HA layer remain on the substrate even after experiencing such a big deformation. Additionally, the surface hardness of the HA layer after SPD is still high at 560 HV (after SPE is 660 HV) as compared to the substrate's 321 HV. This indicates that the thin nano-layer is dense and still strongly intact to the substrate.

3.3. In-vitro analysis

In order to evaluate the biological properties of the HA layer after SPD, the sample is immersed in SBF for a certain duration of time. Fig. 7 shows the HA layer thickness and the surface morphologies before (for the layer thickness image, it is re-produced from Fig. 5b and for the surface morphology, higher magnification image of the surface is re-produced) and after the immersion. As shown in Fig. 7b, before immersion in SBF, the surface morphology of the SPD sample is indicated by the needle-shaped crystals with also fine globular of HA particles and micropores.

After 1 week of immersion, the HA layer thickness increases to approximately 214.7 nm (Fig. 7c). A newly formed layer in the form

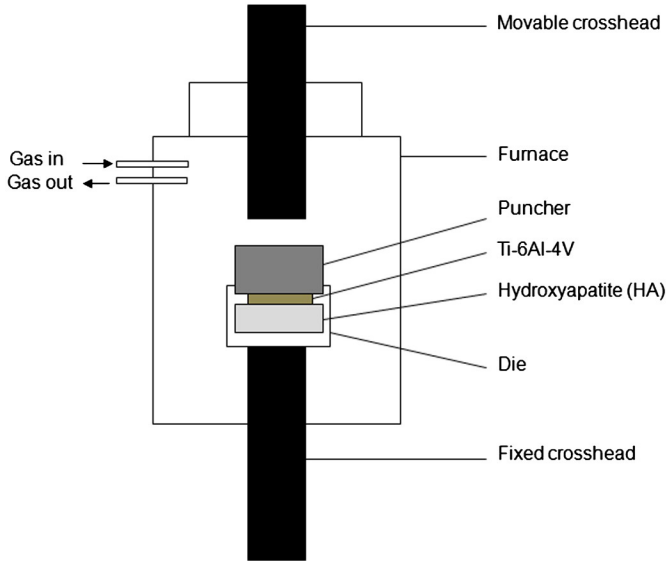

Fig. 1. Schematic diagram of the experimental apparatus.