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Bioactive titanate nanomesh layer on the Ti-based bulk metallic glass by hydrothermal–electrochemical technique

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Abstract

Titanate nanomesh layers were fabricated on Ti-based bulk metallic glass (BMG) to induce bioactivity in the form of apatite-forming ability. Titanate nanomesh layers were prepared by hydrothermal–electrochemical treatment at 90 °C for 2 h, with an aqueous solution of NaOH as an electrolyte. A constant electric current of 0.5 mA cm^{-2} was applied between the BMG substrate and a Pt electrode acting as the anode and cathode, respectively. A nanomesh layer, consisting of nanowires (~20 nm in diameter) formed on the BMG. An immersion test in simulated body fluid for 12 days revealed that the titanate nanomesh layer on the BMG promoted the growth of bone-like hydroxyapatite.

Keywords: Ceramics; Nanostructure; Metallic glass; Titanium alloy; Hydroxyapatite

1. Introduction

A series of Ti-based bulk metallic glasses (BMGs) have been studied extensively due to their excellent mechanical properties, low Young's modulus and high elastic limit [1–6]. However, BMGs contain toxic elements, such as Ni, Al and Be, that exhibit high glass-forming ability [7,8]. The presence of these toxic elements restricts their use in biomedical applications such as load-bearing dental and orthopedic implants.

Recently, Zhu et al. [9] and Qin et al. [10] developed Ti-based BMGs without any toxic elements. However, these may not be directly joined to human bones because of their high chemical stability and bioinertness [6,10,11], which can be overcome by ceramic coating or surface modification of BMGs. Various coating techniques, such as thermal decomposition [12], sputtering [13,14] and micro-arc oxidation [15,16], have been developed to enhance the bioactivity (bone-bonding ability) of Ti alloy implants. However, these coating techniques require high-temperature or high-vacuum conditions that cause cracks in the fabricated films during cooling. Therefore, low-temperature ceramic coatings and surface modification techniques, e.g. alkali heat treatment [17] and sol–gel hydroxyapatite coating [18,19], have been developed for implant materials. For coating or surface modification of BMGs, low-temperature processes are more desirable as such processes maintain their excellent mechanical properties. If not, these BMGs will crystallize, resulting in degradation of their properties.

We have developed a low-temperature hydrothermal–electrochemical method (Fig. 1) for fabricating a crack-free titanate coating on Ti metal and alloys [20–25]. This

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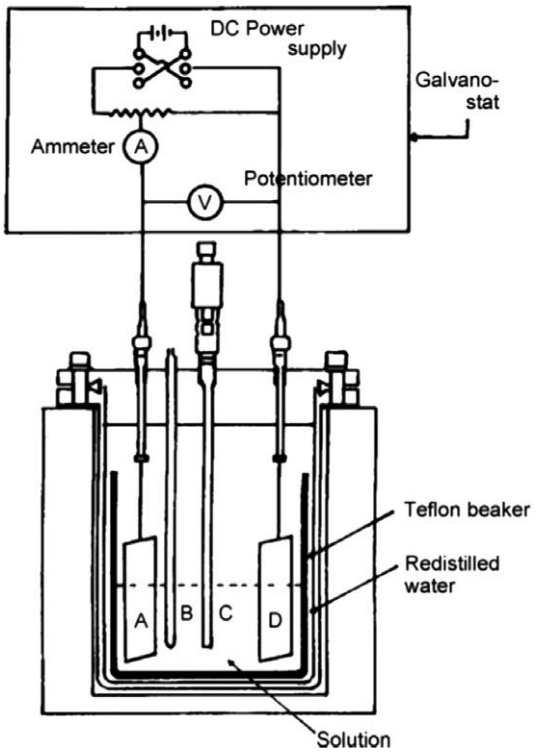

Fig. 1. Schematic illustration of the experimental equipment for the hydrothermal–electrochemical method: (A) cathode (Pt substrate), (B) thermocouple, (C) stirrer and (D) anode (BMG substrate).

method is believed to be one of the most suitable for fabricating bioactive ceramic coatings on BMGs, because the electrochemical reactions allow the formation of ceramics at temperatures below 150 °C. The ceramic and metal layers fabricated by these methods have a widely diffused interface, which should prevent thermal stress accumulation. In these layers, called growing integrated layers (GILs) [26], a compound, most likely an oxide layer, can be rooted in and grown from an active component in an alloy.

Here, as an application of the GIL concept and technology, we demonstrate the direct formation of a bioactive titanate nanomesh layer on a $Ti_{39.6}Zr_{9.9}Cu_{35.6}Pd_{13.9}Ca_1$ BMG, using the hydrothermal–electrochemical technique. This study proposes, for the first time, the possibility of adapting BMGs for biomedical applications by fabricating a titanate nanomesh layer on the Ti-based BMG. Hydrothermal–electrochemical experiments were galvanostatically performed in a NaOH aqueous solution to fabricate a nanomesh layer on the BMG. We also performed the simulated body fluid (SBF) immersion test to determine the bioactivity of the fabricated nanomesh layer.

2. Materials and methods

2.1. Electrode materials

A ribbon-shaped titanium-based BMG ($Ti_{39.6}Zr_{9.9}Cu_{35.6}Pd_{13.9}Ca_1$), fabricated by arc-melting a mixture of pure metal (>99.9%) in an argon atmosphere, was provided by Tohoku University [9] and used as the anode. A platinum substrate (Tanaka Kikinzoku) measuring $10 \times 50 \times 0.5\ mm^3$ was used as the cathode.

2.2. Sample preparation

The Ti-based BMG specimens were cut into $10 \times 50 \times 0.07\ mm^3$ pieces and degreased prior to the hydrothermal–electrochemical experiment. The degreasing was carried out by sonication in acetone for 20 min, rinsing with distilled water, and then drying at ambient temperature. The distance between the electrodes was maintained at 4 cm. The active anodic surface area immersed in the electrolyte was $4\ cm^2$.

The BMG substrates were treated with an aqueous solution of 5 M NaOH (pH 14.5) as the electrolyte, at 90 °C for 2 h, using hydrothermal or hydrothermal–electrochemical techniques. A constant electric current of $0.5\ mA\ cm^{-2}$ was applied between the electrodes during the hydrothermal–electrochemical process. After the hydrothermal or hydrothermal–electrochemical treatment, the specimens were removed, washed with distilled water to remove the alkali, and finally dried at 80 °C for 2 h in air.

2.3. Characterization

X-ray diffraction (XRD) measurements were performed using MXP3VA (MAC Science, Tokyo, Japan), with monochromatized Cu K_α radiation ($\lambda = 1.5418$ Å). The scanning electron microscopy (SEM) images of the specimens were taken with a Hitachi SP 4500 microscope operating at 15 kV. The elemental composition of the titanate nanomesh layer was characterized by energy dispersive X-ray spectroscopy (EDS). The sample surface was analyzed with Raman spectroscopy, using a T64000 Jobin-Yvon spectrometer with an Ar laser (514.5 nm) operated at 50 mW.

2.4. SBF immersion test

The SBF immersion test was carried out to estimate bioactivity, including the hydroxyapatite-forming ability. The SBF was prepared by dissolving reagent-grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in distilled water, and buffering it at pH 7.4 with tris–aminomethane and hydrochloric acid [27]. The ion concentrations and pH of the solution were almost equal to those of human blood plasma. The hydrothermal–electrochemical-treated specimens and bare BMGs were immersed in 30 ml of SBF in a polypropylene vial, and stored in an incubator at 37 °C for 2, 7 and 12 days. The specimen surface was later rinsed with distilled water followed by drying in air.

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