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Effects of solution pH on the structure and biocompatibility of Mg-containing TiO_2 layer fabricated on titanium by hydrothermal treatment

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ABSTRACT

Pure titanium was subjected to surface modification in order to improve its bioactivity. Samples wet-polished by abrasive paper were hydrothermally treated in 0.1 mol/l $MgCl_2$ solutions with different pH values (5.5, 7.5 and 9.5) at 200 °C for 24 h. By forming nano-sized anatase precipitations, hydrothermal treatment increased the thickness of the oxide layer obviously and Mg was found to distribute all through the oxide layer. Treatment in solution with a low pH formed Ti—O—Mg bond as $MgTiO_3$, whereas, high pH induced $Mg(OH)_2$ precipitation onto the samples. Cell attachment and spreading were improved on samples treated in the solution of pH 5.5. As treatment solution pH rose, protein (Bovine Serum Albumin, BSA) adsorption on treated samples increased; however, initial osteoblast attachment and spreading were impaired. It is suggested that, hydrothermal treatment in $MgCl_2$ solution can improve the bioactivity of titanium by immobilizing Mg into oxide layer, however, the chemical state and amount of Mg should be well controlled.

1. Introduction

Titanium is the most widely used metal for endosseous implants in dentistry and orthopedics. However, due to insufficient bioactivity, surface modification is necessary to improve its osseointegration property [1]. It is known that an oxide layer grows spontaneously on the freshly polished surfaces of titanium and its alloys once they were exposed to air. This natural oxide layer has excellent chemical inertness, corrosion resistance and low solubility. The popular application of titanium and its alloys in medical fields over the past decades is thought to be resulted partially from this oxide layer [2]. Furthermore, studies of *in vitro* apatite formation and histological observations of interface between bone and titanium implant suggested that the oxide layer played a vital role in the reactions between implant and bone [3–5]. However, the naturally formed oxide layer on titanium is typically very thin, less than 10 nm, has a high density of structural defects and is generally not thought to be bioactive enough [6]. Improved bioactivity has been reported by fabricating oxide layer with better structure using sandblast-acid etching, TiO_2 plasma spray and electrochemical oxidation, *etc.* [7–9].

Modifications of the titanium oxide layer with bioactive elements such as Ca, P and F have also been widely reported [10–12]. Both *in vitro* and *in vivo* results have shown that surface osteoconductivity of titanium was obviously improved by inducing such elements. Magnesium (Mg) is the fourth most abundant mineral in human body and the most abundant intracellular divalent cation with essential roles in many physiological functions related to bone remodeling [13–15]. Incorporations of Mg into alumina and titanium implants by ion implantation and electrochemical oxidation have been reported to significantly improve cell responses and increase bone-implant contact [16,17]. Our previous study also showed that Mg-containing titanium oxide layer fabricated by hydrothermal treatment could significantly enhance osteoblast attachment, spreading and subsequent proliferation on titanium [18].

Compared with ion implantation that requires complicated apparatus, hydrothermal treatment is more feasible and economical. However, in previous reports, the amounts of bioactive elements combined into oxide layers by hydrothermal treatment in slightly acidic solution were found to be quite limited [18–20]. Hydrothermal synthesis of TiO_2 and alkaline-earth titanates was proved to be a dissolution–precipitation process and the reaction could be promoted by increasing basicity of solution [21]. Therefore, in this study we carried out hydrothermal treatment of pure titanium in magnesium chloride ($MgCl_2$) solution with different pH values and fabricated titanium oxide layers with low, medium and high Mg levels. Surface properties and structure of oxide layers were investigated and the effects of different levels of Mg incorporated into titanium oxide layer on short-term osteoblast–material interactions, including cell attachment and spread, were also determined.

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2. Materials and methods

2.1. Hydrothermal treatments

Pure titanium (The Niraco Co., Tokyo, Japan) discs, 15 mm in diameter and 1 mm in thickness, were wet-polished with SiC abrasive paper up to 1000 # and then ultrasonically washed with acetone and distilled water before treatment. Hydrothermal solutions were prepared by dissolving reagent grade $MgCl_2$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan) into distilled water with the concentration of 0.1 mol/l (pH 5.5). pH values of another two groups of solutions were adjusted to 7.5 and 9.5, respectively, by adding diluted NaOH solution while being continuously stirred. 10 ml solution for each sample was filled into Teflon-lined vessels with stainless steel jackets and reactions were carried out in an oven at 200 °C for 24 h. After cooling down, samples were taken out, rinsed thoroughly and then ultrasonically washed in distilled water for 10 min. Samples were coded according to the treatment solution pHs, namely, Mg(low)–Ti for samples treated in solution of pH 5.5, Mg(med)–Ti for pH 7.5 and Mg(high)–Ti for pH 9.5, respectively. Wet-polished samples without hydrothermal treatment (UnTi) were used as controls.

2.2. Surface characterizations

Surface morphologies of samples before and after treatment were observed with scanning electron microscope (SEM, S-3100, Hitachi Co., Japan). Wettability was evaluated by measuring contact angles with distilled water on a contact angle meter (DM 500, Kyowa Interface Science Co., Ltd., Japan). Surface roughness was analyzed by color 3D laser scanning microscope (VK9710, Keyence Co., Japan). Surface chemical compositions were investigated by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Fisher Scientific, UK). All the spectra were calibrated by setting hydrocarbon C 1s to 284.8 eV. Ar ion etching was performed on surfaces and element distribution information was collected. The etching rate was 1.8 Å/s as calibrated using SiO_2. The surface crystal structures of samples were analyzed by Laser Raman Micro-Spectroscopy (NRS-5100, JASCO Co., Ltd, Japan). Mg release was investigated by immersing samples into 5 ml NaCl solution (0.9%, wt/vol) at 36.5 °C up to 7 days and Mg ion concentrations were measured

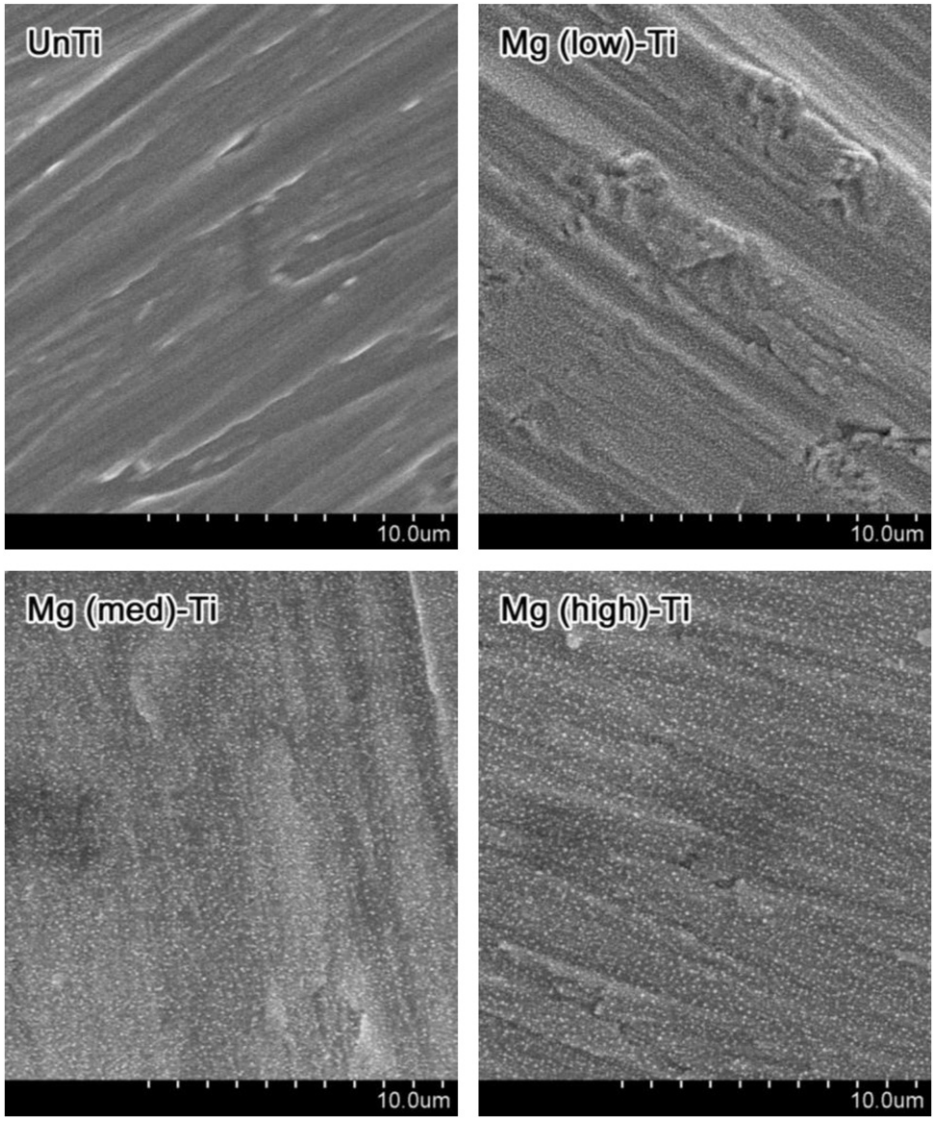

Fig. 1. SEM images of different samples.