Water Glass Coating on a Ti Substrate to Form Si-OH Groups for Improving Cell Behaviors of Dental Implants

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Abstract: Some biomaterials bond with the surrounding living bone through a bone-like apatite layer which is formed on their surfaces in the human body. The existence of functional groups such as Si-OH and Ti-OH on the Ti surface accelerates the formation of a bone-like apatite layer in simulated body fluid (SBF) solution. In this study, Si-OH functional groups were formed on the Ti surface by water glass (WG, sodium silicate) coating and subsequent HCl treatment. The thickness of the WG layers increased with an increasing concentration of WG solution and the number of WG coatings. The chemical composition of the WG coated layers changed from sodium silicate to pure silica by the HCl treatment via ion-exchange. The content of hydroxyl groups on the HCl-treated samples was confirmed by TFAA treatment using XPS. The amount of hydroxyl groups on the Ti surface depended upon the vol% of WG and the number of WG coatings. The higher the concentration of WG and the greater the number of WG coatings, the more hydroxyl groups existed on the Ti surface. The cell (MSC) proliferation on the WG coated Ti was significantly improved compared to the non-WG coated sample due to the formation of hydroxyl groups on the WG coated Ti. The cell proliferation also depended on the WG coating thickness and the number of hydroxyl groups on the surface. That is, the increase in the number of hydroxyl groups on the Ti surface afforded by the WG coating resulted in better cell behavior. We conclude that Ti coated with WG can be employed for the early fixation of dental implants.

1. INTRODUCTION

Ti and titanium alloys are commonly used as a material for orthopedic and dental implants, due to their outstanding corrosion resistance and good biocompatibility. However, they require a long period of time to bond with the surrounding living bone. In order to enhance the early fixation and osseointegration with the surrounding bone tissue in the human body, various coatings on the Ti surface have been studied for many years [1-3].

It has been reported that Ti and its alloys form a bone-like apatite layer on their surfaces in a simulated body fluid (SBF) when they are exposed to NaOH aqueous solution and subjected to subsequent heat treatment. These NaOH and heat-treated metals easily form apatite in the living body and bond to bone through the apatite layer, as in SBF [4,5]. It is known that the existence of functional groups such as Si-OH and Ti-OH on the Ti surface accelerates the formation of a bone-like HAp layer in SBF solution [6,7].

Water glass is a well-known material which is widely used as an adhesive agent and easily adheres to substrates upon heating at relatively low temperatures. In addition, silica glass derived from water glass easily releases soluble silica in aqueous solution and includes plentiful silanol functional groups (Si-OH) on its surface, which has been reported to lead to HAp nucleation in a body fluid [8,9].

In this study, a WG coating was applied to form Si-OH groups on the Ti surface. The WG coated Ti discs were characterized by SEM and EDS for the examination of the surface morphology and chemical composition, respectively. After the surface treatments, cell culture experiments were conducted for 2 hrs and 1 and 5 days [10].

2. EXPERIMENTAL PROCEDURES

Commercially pure Ti discs (grade 4) were polished using a series of SiC grit papers (Daesung, Korea). The polished samples were blasted using 250–300 μm HAp grits and then washed with 1 vol% HCl aqueous solution in an ultrasonic bath for 2 mins to remove the impurities and HAp residues on the cp-Ti disc surfaces. The samples were cleaned in an ultrasonic bath again to remove the HCl residues on the Ti discs. The washed samples were etched by alkali treatment in 5 M NaOH solution for 24 hrs and
Table 1. Various samples prepared for comparison of surface characteristics and cell behaviors

<table>
<thead>
<tr>
<th>Sample nomenclature</th>
<th>WG coated</th>
<th>HCl etched</th>
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<tbody>
<tr>
<td>Blasted B</td>
<td>W15-1</td>
<td>W15-1e</td>
</tr>
<tr>
<td>BN</td>
<td>W15-2</td>
<td>W15-2e</td>
</tr>
<tr>
<td>BNH</td>
<td>W15-3</td>
<td>W15-3e</td>
</tr>
</tbody>
</table>

(1) B: blasted with 250–300 μm HAp grits
(2) BN: blasted and then etched with 5 M NaOH
(3) BNH: blasted, NaOH etched and then heat-treated at 600 ℃ for 1 hr
(4) W15-1: once coated BNH with 15 vol% WG and heat-treated at 300 ℃ for 2 hrs
(5) W15-2: twice coated BNH with 15 vol% WG and heat-treated at 300 ℃ for 2 hrs
(6) W15-3: 3 times coated BNH with 15 vol% WG and heat-treated at 300 ℃ for 2 hrs
(7) W15-1e: etched W15-1 with 0.1M HCl
(8) W15-2e: etched W15-2 with 0.1M HCl
(9) W15-3e: etched W15-3 with 0.1M HCl

then cleaned in an ultrasonic bath. The washed samples were heat-treated at a rate of 5 ℃/min and kept at 600 ℃ for 1 hr. The preparation procedure of the Ti substrates is shown in Fig. 1.

The heat-treated samples were coated with 10, 15, and 20 vol% WG (mNa₂OₙSiO₂·(100-m-n)H₂O, where m = 9.0–10.0, n = 28–30.0, S-Chemtec, Korea) solutions using a spin coater at 5000 rpm for 1 min, respectively. The WG coating was applied once, twice, and three times on the prepared Ti using each prepared WG solution. The dried WG coated Ti discs were heat-treated at a rate of 0.5 ℃/min and kept at 300 ℃ for 2 hrs. After the heat treatment, the samples were etched in 0.1 M HCl aqueous solution for 1 hr in an ultrasonic bath glass to form Si-OH functional groups on the Ti discs by etching the Na₂O out of the WG.

For the comparison of the surface characteristics and cell behaviors, various samples were prepared, as shown in Table 1, where sample B is the Ti disc blasted with 250–300 μm HAp grits, sample BN corresponds to sample B etched with 5 M NaOH, and sample BNH corresponds to sample BN heat-treated at 600 ℃ for 1 hr. Samples W15-1, W15-2, and W15-3 are coated with 15 vol% WG once, twice, and three times, respectively, and then heat-treated at 300 ℃ for 2 hrs. Samples W15-1e, W15-2e, and W15-3e correspond to samples W15-1, W15-2, and W15-3 etched with 0.1 M HCl, respectively.

The prepared samples were examined using FE-SEM (field emission scanning electron microscopy, Hitachi, Japan) to observe the surface microstructures and EDS (energy dispersive X-ray spectroscopy, Hitachi, Japan) to confirm the chemical composition.

The surface layers of the prepared samples were examined using TF-XRD (thin-film X-ray diffraction, PANalytical, Netherlands) to identify the phases on the surface treated Ti specimens. The Si-OH functional groups formed on the Ti surfaces were confirmed using XPS (X-ray photoelectron spectroscopy (ULVAC-PHI, Japan). For the qualitative and quantitative analyses of the Si-OH groups, the saturated vapor of trifluoroacetic anhydride (TFAA) was reacted with the hydroxyl groups on the Ti surface at 25 ℃ for 15 minutes in order to replace the OH groups with F ions [11]. The concentration of F ions on the TFAA treated Ti substrate was measured using XPS.

For the cell attachment and proliferation analysis, mesenchymal stem cells (MSCs) were isolated from the aspirated iliac crest of normal human donors through a protocol approved by the Internal Review Board of Yeungnam University Hospital using methods described previously [12]. The MSCs were cultivated with DMEM (Gibco-BRL, MD, USA) supplemented with 10% FBS (Gibco-BRL) and 2-3 passage cells were used for the cell experiments. Ethylene