HYDROXYAPATITE COATING AND SBF IMMERSION TEST OF SURFACE MODIFIED TITANIUM BY WET CHEMICAL METHOD

Yutaka Honda, Masahiro Inuzuka, *Satoshi Nakamura, Kimihiro Yamashita

(*Corresponding author: nakamura.bcr@tmd.ac.jp)
Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University
2-3-10 Kanda-Surugadai, Chiyoda, Tokyo 101-0062, Japan

Keywords: Hydroxyapatite, surface modified titanium, wet chemical method, simulated body fluid (SBF)

Hydroxyapatite coating (HA-C) material has been applied as orthopedic and dental implant, and we have investigated several properties of hydroxyapatite coating (HA-C) on titanium (Ti) substrate. Recently, in order to shorten the period until osteointegration and to increase the bone contact rate, surface modification of Ti and its alloys have been reported. However, Ti was used as a substrate in this study. Ti surface was modified by concentrated NaOH solution and subsequent heat treatment. The surface modified substrate was soaked into calcium and phosphate solutions to obtain apatite coating layer. The obtained layer was verified to hydroxyapatite (HA) by fourier-transform infrared spectroscopy (FT-IR) and thin-film X-ray diffractometry (TF-XRD). The bioactivity of this coating layer has been confirmed by the simulated body fluid (SBF) immersion.

(Received June 30, 2004; Accepted August 30, 2004)

INTRODUCTION

Titanium (Ti) and its alloys are widely used as implant materials because of their high toughness and excellent biocompatibility1. However, Ti metal cannot directly bond with living bone2, and it has been known that their biocompatibility is lower than that of hydroxyapatite (HA). In order to shorten the period until osteointegration and to increase the bone contact rate, several surface modification methods of Ti have been reported. Representative methods are sandblasting3, acid-etching 4, and Ti plasma spraying5. Besides these methods, Uchida et al. reported that Ti and its alloys form a typical bone-like apatite which on their surfaces in a simulated body fluid (SBF), when they are subjected to NaOH and subsequent heat treatments6. Based on animal experiments, Kokubo et al. also reported that these surfaces directly bonded to bone without intervening layer, but with Ti-OH groups obtained by NaOH- and heat-treatments7,8. As mentioned before, they and other researchers have tried to use bioactivity of surface modified Ti and its alloys as implant material, however we considered that surface modified Ti and its alloys could obtain HA coating (HA-C) on its surface by wet chemical method. One of the simple wet methods to coat HA is alternate soaking method5-8. In this method, Taguchi et al. reported that HA could be formed in the desired amount on the three-dimensional structured organic matrix at normal temperatures and pressure in vitro using this method.

In this study, we tried to obtain HA layer on the surface modified Ti substrate, and analyzed the biocompatibility of the obtained layer by SBF immersion test. The surface of Ti substrate was modified by NaOH- and heat-treatment, and in order to prepare HA layer, wet chemical method was performed refer to alternate soaking method5-8.

MATERIALS AND METHODS

Commercially pure Ti metal was firstly abraded with No. 120 silicon carbide emery paper (CARBIMET®, Buehler; Illinois, USA), then it was ultrasonically washed with acetone, and pure water for 30 min each. After those polishing and washing processes, it was dried at room temperature, then it was soaked into 5M NaOH at 60°C for 24h. The specimen was then washed with distilled water and soaked into distilled water at 80°C for 48h. After those processes, it was heated at 600°C for 1h. The NaOH- and heat-treated Ti is abbreviated to A-Ti in this paper. In preparation of HA-C on Ti substrate, A-Ti was used as a substrate. Firstly, the substrate was soaked in CaCl₂ (200mM/buffering the solution to pH 7.40 with (CH₂OH)₃CNH₃-HCl) at 37°C for 30 min. After it was dried at air atmosphere, it was then soaked in Na₂HPO₄ (120mM/buffering the solution to pH 7.40 with same buffer as the case of CaCl₂) at 37°C for 30 min. After it was dried at room temperature, it was then soaked in Na₂HPO₄ (120mM/buffering the solution to pH 7.40 with same buffer as the case of CaCl₂) at 37°C for 30 min. The substrate was then washed with distilled water, and dried at room temperature to complete the preparation of HA. The prepared layer is abbreviated to W-Ti. W-Ti was analyzed by fourier-transform infrared spectroscopy (FT-IR: Diamond20, JEOL Co., Tokyo, Japan). The coated layer was firstly scraped off, diluted with KBr, and was measured. The surface layer of W-Ti was also analyzed using thin-film X-ray
Hydroxyapatite Coating and SBF Immersion Test of Surface Modified Titanium by Wet Chemical Method

diffractometry (TF-XRD: RTP500, Rigaku Co., Tokyo, Japan). TF-XRD measurements on the surface of W-Ti was performed with using Cu-Kα X-ray source at 50kV and 100mA with a step rate of 2θ= 6°/min, and θ = 2° glancing angles against the incident beam. W-Ti was immersed into SBF to analyze its biocompatibility. SBF is the solution which ion concentrations and pH nearly equal to those in human blood plasma at 36.5°C. In this study, we applied 1.5 SBF which ion concentrations were 1.5 times denser than SBF. It was prepared by dissolving reagent-grade NaCl, KCl, KH2PO4·3H2O, MgCl·6H2O, CaCl2, and Na2SO4 in ultra-pure water and buffering the solution to pH 7.4 with (CH2OH)3CNH3 and HCl. W-Ti was immersed in 1.5 SBF for 24h, and it was analyzed by TF-XRD with same condition that applied to the measurement of W-Ti. The surfaces of abraded Ti, NaOH- and heat-treated Ti, W-Ti, and W-Ti which immersed in 1.5 SBF for 24h were observed by scanning electron microscopy (SEM: JEOL JSM-6300).

RESULTS AND DISCUSSIONS

The SEM photographs of abraded Ti, A-Ti, W-Ti surfaces, and the surface of W-Ti after immersion of 1.5 SBF for 24h are shown in Figure 1 (A)-(D) respectively. Based on the SEM observation, the surface of A-Ti (Fig. 1 (B)) was remarkably changed its surface morphology compared with abraded Ti (Fig. 1 (A)) by NaOH- and heat-treatments. After these treatments, abraded Ti surface was lost its dense morphology, and showed a porous network structure. After soaking in CaCl2 and Na2HPO4 solutions of A-Ti, the surface was covered with white layer, and was visible to naked eye. SEM observation showed that this obtained layer of W-Ti (Fig. 1 (C)) was spongy shape, and it was completely covered up the surface of NaOH- and heat-treated Ti substrate.

FT-IR spectra of W-Ti and HA powder are shown in figure 2. The strong absorbance peaks were broadly observed at 1030 cm⁻¹ and 560 cm⁻¹ on W-Ti coating layer that due to stretching and venging vibration of PO₄³⁻ respectively, as also observed sharply on the spectrum of HA phase. These results showed that the obtained layer contained PO₄³⁻ and its structure could be similar to that of HA. However, the sharp peak which characteristic for HA spectrum and due to stretching vibration of OH⁻ was not observed at around 3570 cm⁻¹ on W-Ti. The reason why the absorption peak of OH⁻ was not observed on W-Ti is...
Honda Y, Inuzuka M, Nakamura S, Yamashita K considered that the amount of OH⁻ ions were small, and were not detected. From absorbance peaks of PO₄³⁻ were broadly observed, therefore the structure of obtained layer was considered that it was not uniform.

TF-XRD patterns of W-Ti and W-Ti after immersion of 1.5 SBF for 24h are shown in figure 3. At 31.776°, the strongest peak which due to (211) of HA and hard to divide in two peaks, but (112) of HA was also observed. The sharp peak was observed at 25.284° with this clear peak, shoulder was also observed at 25.992° which due to (002) of HA (JCPDS 09-0432). On the other hand, after immersed in 1.5 SBF for 24h, the diffraction pattern was changed. The peak of anatase at 25.284 was decreased, and (002) plane of HA was obviously increased. Around 32°, the peak resulted from bone-like apatite which crystallized under 1.5 SBF was obtained as a broad peak.

Based on result of TF-XRD, the obtained layer was assigned as HA. In FT-IR measurements, several absorbance peaks that due to PO₄³⁻ were broadly observed, and the sharp peak due to OH⁻ which characteristic for HA was not observed. From these aspects, even though TF-XRD pattern showed HA pattern, possibly the obtained HA phase was low-crystallinity, and was not uniform.

This obtained HA layer could be prepared by firstly inducement of Ca²⁺ ions on the A-Ti surface when it was soaked in CaCl₂ solution. Then, PO₄³⁻ ions were induced to vicinity of A-Ti surface when it was soaked in Na₂HPO₄ solution, and were reacted with Ca²⁺ ions to form HA.

After 1.5 SBF immersion of W-Ti for 24h, the surface was covered with bone-like apatite crystals, as it was shown in Figure 1 (D). It showed that the spongy morphology of W-Ti surface layer was completely filled up with bone-like apatite crystals. From TF-XRD measurement, the diffraction pattern was different from before immersion. The (002) of HA was highly increased, and broad peak was observed at around 32°. The results gave that the bone-like apatite crystals were obtained within 24h on W-Ti surface, therefore, the obtained HA phase possessed excellent bone-like apatite formability. The obtained HA phase, which prepared by the simple wet chemical method is expected to shorten the period until osteointegration, and increase bone contact rate.

CONCLUSION

Commercially pure Ti surface was firstly modified by NaOH- and heat-treatments. The NaOH- and heat-treated Ti was used as a substrate of HA-C. The substrate was soaked in CaCl₂ and Na₂HPO₄ solutions for 30 min respectively to obtain HA. The surface of substrate was covered with spongy shape layer. This layer was verified as HA by the FT-IR and TF-XRD measurements. However, its crystal structure was possibly not uniform. By 1.5 SBF immersion, bone-like apatite crystals were filled up its spongy coating layer within 24h. From this aspect, this HA layer possesses high bioactivity.

REFERENCES

Hydroxyapatite Coating and SBF Immersion Test of Surface Modified Titanium by Wet Chemical Method


