

High Hydroxyapatite-forming Ability on TiO₂ Scale Fabricated by Heat Treatment of Ti

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Titanium (Ti) is widely used for artificial joints because of its high fracture toughness and good biocompatibility. However, Ti does not bond to living bone, and thus, its fixation to the surrounding bone is not stable over the long term. Several methods have been developed to impart Ti with bone-bonding ability. Wang et al. improved the hydroxyapatite-forming ability of Ti through a titanium oxide (TiO₂) scale produced by heat treatment of Ti [1]. In general, bioactive materials in the body bond to living bone through this hydroxyapatite layer. Hydroxyapatite formation is a complex process that involves controlled nucleation and growth from an aqueous solution. Once hydroxyapatite nuclei are formed, they grow by the uptake of calcium and phosphate ions from the solution.

Recently, we have shown that heat treatment of Ti in a nitrogen atmosphere with a precisely regulated oxygen partial pressure (P_{O_2}) of 10^{-14} Pa at 973 K for 1 h strongly enhanced hydroxyapatite formation compared with that in air with a P_{O_2} of 10^4 Pa [2]. A rutile-type TiO₂ scale was formed on the Ti surfaces when the Ti was heated with a P_{O_2} of either 10^{-14} and 10^4 Pa. However, the hydroxyapatite formation kinetics, described using the Avrami-Erofeev equation, on the TiO₂ scale had a significant dependence on the P_{O_2} in the nitrogen atmosphere. Following heat treatment with a P_{O_2} of 10^{-14} Pa at 973 K for 1 h, the Avrami index for the scale, which was soaked in a simulated body fluid (SBF) with ion concentrations nearly equal to those in human blood plasma as the medium for hydroxyapatite nucleation at 309.5 K, was $n=2$. This implies the instantaneous nucleation of hydroxyapatite, which completely covers the scale surface in a short time. By contrast, in the case of treatment in air with a P_{O_2} of 10^4 Pa at 973 K for 1 h, the Avrami index for the scale was $n=3$. This means that the hydroxyapatite nuclei were sparsely distributed, and formed at a constant rate, taking a long time to cover the scale surface [3]. However, the relationship between the microstructure of the TiO₂ scale and the enhancement of hydroxyapatite formation remains unclear.

The present study examined the factors governing hydroxyapatite formation by characterizing the microstructure of the TiO₂ scale and investigating the process of hydroxyapatite nucleation. Figure 1 shows a cross-sectional transmission electron microscopy (TEM) image of TiO₂ scale on a Ti surface treated in nitrogen with a P_{O_2} of 10^{-14} Pa at 973 K for 1 h, and the corresponding secondary ion mass spectroscopy (SIMS) depth profiles for N and O. The TiO₂ scale had a layered nitrogen-doped rutile-type TiO₂ (surface side)/TiN (substrate side) structure. The scale thickness was around 100-200 nm. The peaks of N K-edge electron energy loss spectroscopy (EELS) of the scale were different from that for a nitrogen-doped TiO₂ photocatalyst, in which nitrogen was substituted at oxygen sites in TiO₂ [4-5]. In contrast, in the case of treatment in air with a P_{O_2} of 10^4 Pa at 973 K for 1 h, the top surface layer of the scale

was composed of rutile-type TiO_2 containing a small amount of nitrogen, and the total thickness of the scale was about $1\ \mu\text{m}$.

The surface charge on scales formed by treatment in nitrogen with a P_{O_2} of 10^{-14} Pa was strongly positive, with a zeta potential of approximately 20 mV, whereas for a P_{O_2} of 10^4 Pa, the zeta potential was close to zero. To investigate the early stages of hydroxyapatite nucleation, the elemental and molecular compositions of precipitates formed on samples treated in nitrogen with a P_{O_2} of 10^{-14} Pa after being soaked in SBF from 1 min to 4 h were identified by time-of-flight secondary ion mass spectroscopy (ToF-SIMS). It was found that phosphate ions were predominantly adsorbed, followed by calcium ions. The P/Ca peak intensity ratio decreased with increasing soaking time in SBF, reaching almost 2.48, which is the stoichiometric value for sintered hydroxyapatite.

These results show that the strongly positively charged surface of the scale formed on the sample treated in nitrogen with a P_{O_2} of 10^{-14} Pa can effectively promote the formation of hydroxyapatite nuclei. This occurs by the initial attraction of negatively charged phosphate ions, followed by positively charged calcium ions.

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References

- [1] X. X. Wang et al., *Biomaterials* **24** (2003) 4631.
- [2] M. Hashimoto et al., *J. Mat. Sci. Mat. Med.*, **22** (2011) 2013.
- [3] M. Hashimoto et al., *Mat. Sci. Eng. C* **33** (2013) 4155.
- [4] R. Asahi et al., *Science*, **293** (2001) 269.
- [5] T. Yoshida et al., *Trans Mat. Res. Soc. Japan*, 33[2] (2008) 339.

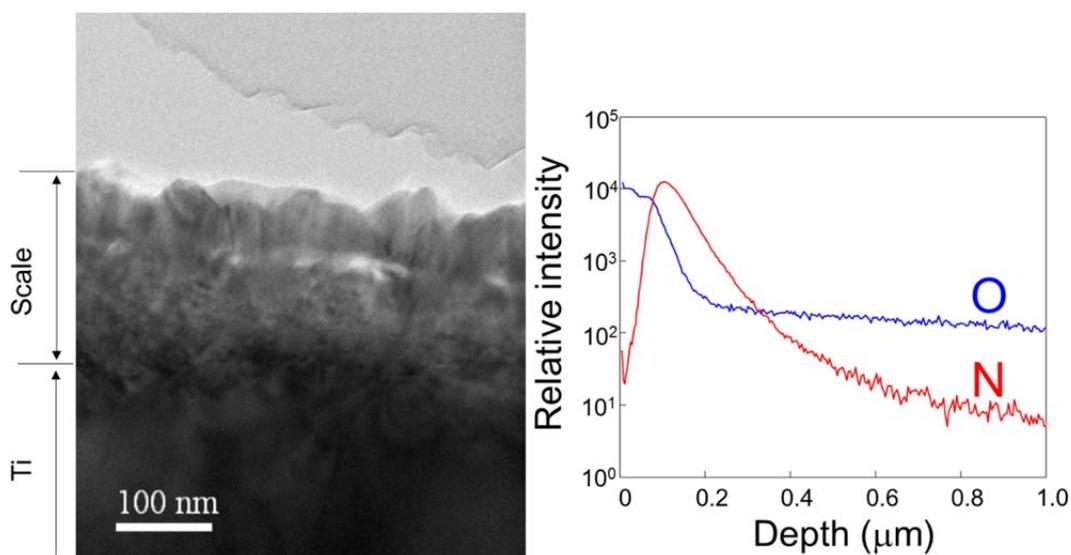


FIG. 1. Cross-sectional TEM image and SIMS depth profiles of N and O in the scale formed by treatment in nitrogen with a P_{O_2} of 10^{-14} Pa at 973 K. The SIMS intensity is normalized by that for Ti.