

# Bioactive Titania Layer Fabricated on Metallic Biomaterials by Electrodeposition

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**Abstract** Improvement of bone integration ability of metallic biomaterials is needed for long-term stable fixation to bone tissues. Essential prerequisite for materials to show bone-integrating bioactivity is formation of apatite layer on their surfaces in body environments. Several functional groups have potential to trigger the apatite nucleation. In the present study, we attempted fabrication of bioactive titania layer which provides Ti-OH groups effective for the apatite formation on bioinert metals such as stainless steel and Co-Cr-Mo alloys by electrodeposition. Their bioactivity was evaluated *in vitro* in simulated body fluid (SBF). Bioactive titania layer was fabricated on both metals after heat treatment at appropriate temperature. Co-Cr-Mo alloys showed a tendency to form larger amount of the apatite than the stainless steel at the same temperature of heat treatment. This phenomenon was attributed to intergranular corrosion on the stainless steel and apatite deposition on the heat-treated stainless steels without the titania coating.

**Keywords** Metallic biomaterials, Titania, Apatite, Bioactivity, Electrodeposition, Simulated body fluid (SBF)

## 1. INTRODUCTION

Metallic biomaterials have excellent strength and fracture toughness. Therefore they are clinically used for biomedical application under loaded conditions such as artificial joints and artificial tooth roots [1]. However they themselves do not show bone-bonding bioactivity. Improvement of the bioactivity of metals is needed for long-term stable integration to bone tissues.

Essential requirement for artificial materials to show the bioactivity is formation of apatite layer on their surfaces in body environments [2]. Several functional groups such as Si-OH, Ti-OH, Zr-OH, Ta-OH have potential to trigger the apatite nucleation [3]. In order to prepare bioactive metals utilizing titania phase abundant in Ti-OH groups, several techniques such as chemical modification of Ti metals and its alloys have been reported [4-6].

In the present study, we attempted fabrication of bioactive titania layer on bioinert metals such as stainless steel and Co-Cr-Mo alloys by electrodeposition of titania layer. It is reported that alkali and heat treatment is not effective for providing these metals with bioactivity [4]. Their bioactivity was evaluated *in vitro* in simulated body fluid (SBF). Bioactivity of artificial materials can be well evaluated in terms of the apatite deposition in SBF [7].

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Specimen

Stainless steel SUS316 and Co-Cr-Mo alloy were polished by emery paper and subsequently diamond paste with 1  $\mu\text{m}$  in particle size. Rectangular specimens 10 x 100 x 0.1 mm in size were used for SUS316, whereas disk specimens with 15 mm in diameter and 1 mm in thickness for Co-Cr-Mo alloy. The specimens were fixed on the cathode and soaked in titanium bis(ammonium lactato) dihydroxide  $((\text{CH}_3\text{CH}(\text{O})\text{CO}_2\text{NH}_4)_2\text{Ti}(\text{OH})_2)$  aqueous solution at 5 mass%. DC voltage ranging 100 to 130 V was applied to the specimens for 5 min. Meanwhile current density was fixed at around 1 A/cm<sup>2</sup>.

The specimens were then heated at various temperatures ranging 300 to 800°C at a rate of 10°C / min and kept at each temperature for 1 h.

### 3.2 Evaluation of Specimen

Adhesion of the titania layer to the substrates was measured by peeling-off test using Scotch<sup>®</sup> tape according to ASTM D3359-87. Namely, the specimen surface was cross-cut with a stainless steel knife at interval of 1 mm. Number of the square peeled off was counted.

The specimens were then soaked in SBF ( $\text{Na}^+$  142.0,  $\text{K}^+$  5.0,  $\text{Mg}^{2+}$  1.5,  $\text{Ca}^{2+}$  2.5,  $\text{Cl}^-$  147.8,  $\text{HCO}_3^-$  4.2,  $\text{HPO}_4^{2-}$  1.0 and  $\text{SO}_4^{2-}$  0.5 mol·m<sup>-3</sup>) at 36.5°C for 7 days. As a reference, stainless steel substrates subjected to mere heat treatment at 400°C without electrodeposition of titania were also soaked in SBF. Surface structure of the specimens was analyzed by scanning electron microscopic (SEM) observation and thin-film X-ray diffraction (TF-XRD) and energy-dispersive X-ray spectroscopy (EDX).

## 3. RESULTS

Figure 1 shows TF-XRD patterns of the surfaces of SUS316 and Co-Cr-Mo alloys which were subjected to electrodeposition and heat treatments at various temperatures. Formation of anatase was observed at 400°C. Conversion of the anatase into rutile initiated at 600°C.

Table 1 shows results of cross-cut adhesion test of the specimens, which was confirmed by SEM observation. Adhesion of the surface layer on both the metals is enhanced by heat treatment at temperature ranging 400 to 700°C.

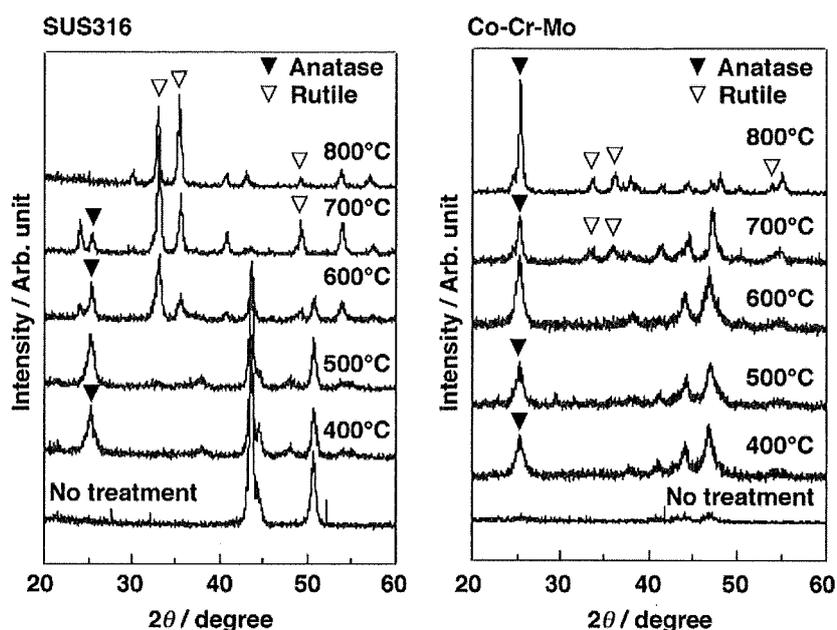


Figure 1 TF-XRD patterns of the surfaces of SUS316 and Co-Cr-Mo alloys which were subjected to electrodeposition and heat treatments at various temperatures.

Table 1 Results of cross-cut adhesion test of the specimens, which was confirmed by SEM observation

Temperature / °C	Substrate	
	SUS316	Co-Cr-Mo
300	D	C
400	B	B
500	B	A
600	A	A
700	A	A
800	C	C

Area ratio of peeled surface to substrate is A: 0%, B: <5%, C: 5-15%, D: 15-35%.

Figure 2 shows TF-XRD patterns of the surfaces of Co-Cr-Mo alloys which were subjected to electrodeposition and heat treatment at 600°C and subsequently soaked in SBF for 7 days. Tiny broad peaks as signed to low-crystalline apatite were detected at 26° and 32° in 2θ. Tendency for the apatite formation on all the specimens in SBF was summarized in Table 2.

Figure 3 shows SEM photograph of the surface of stainless steel subjected to heat treatment at 400°C and soaked in SBF for 3 days. Apatite deposition was observed partially on the substrate. It is noted that the apatite was vigorously deposited along the narrow scratches.

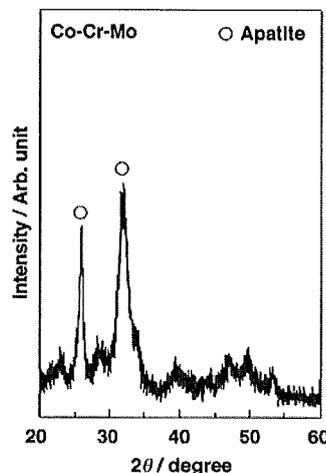


Figure 2 TF-XRD patterns of the surfaces of Co-Cr-Mo alloys which were subjected to electrodeposition and heat treatment at 600°C and subsequently soaked in SBF for 7 days.

Table 2 Tendency for the apatite formation on the metals electrodeposited with titania after soaked in SBF for 7 days, which was confirmed by SEM observation

Temperature / °C	Substrate	
	SUS316	Co-Cr-Mo
300	C	C
400	A	B
500	B	A
600	D	A
700	D	C
800	D	C

Area ratio of deposited apatite to substrate is A: 65-100%, B: 35-65%, C: 5-35%, D: <5%.

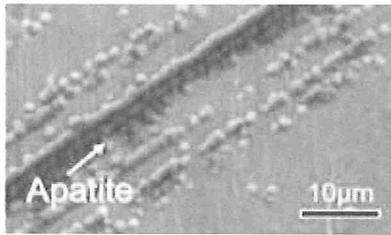
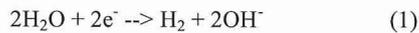


Figure 3 SEM photograph of the surface of stainless steel subjected to heat treatment at 400°C and soaked in SBF for 3 days.

#### 4. DISCUSSION

Crystalline titania films were formed on stainless steels and Co-Cr-Mo alloys by electrochemical deposition on the cathode in water-soluble titanium compound and subsequent heat treatment (See Fig. 1). Hydroxide ions are formed on the cathode by the following chemical reaction:



It would be assumed that the titanate ions dissociated from the titanium bis(ammonium lactato) dihydroxide diffuse into the cathode side, and its hydrolysis is enhanced by the OH<sup>-</sup> ions [8].

The prepared titania films has potential to form the apatite in SBF (See Fig. 2 and Table 2). Comparing the apatite-forming ability of the specimens heated at 600°C, SUS316 showed lower ability than Co-Cr-Mo alloy. Amount of Ti-OH groups on the surfaces would be almost the same for both specimens after heated at 600°C. It is known that intergranular corrosion occurs on the stainless steel above 550°C. The above difference would be attributed to the intergranular corrosion.

There is another factor affecting the apatite deposition in SBF. As shown in Fig. 3, even mere heat-treated stainless steel can form the apatite in SBF. It would be assumed that apatite deposition is achieved not only on the titania films but also on the substrates without the titania coating, and therefore relative amount of the deposited apatite on the titania layer is low in the case of the stainless steel.

Notably, the apatite formation is vigorous along the narrow scratches in the specimen. Sugino *et al.* proposes enhanced effect of the apatite deposition in spatial gaps of heat-treated titanium metals and its alloys in SBF [9]. The results in this study suggest that this type of "Spatial gap effect" can be also observed on the stainless steels. Precise mechanism should be clarified in near future.

This type of electrodeposition technique is applicable for various functionalization of metal implants. For example, deposition of ceramics with high hardness would produce novel implant materials with high wear resistance.

#### 5. CONCLUSION

Titania layer was formed on metal substrates such as stainless steel and Co-Cr-Mo alloy by electrodeposition process. The metals deposited with the titania layer formed the apatite on their surfaces in SBF, when it was heat-treated at appropriate temperature. This technique is expected to be applicable for various kinds of functionalization of metallic implants.

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#### References

- [1] B.D. Ratner, A.S. Hoffman, F.J. Schoen, J.E. Lemons, "Biomaterials Science 2nd Edition", Elsevier Academic Press, Amsterdam (2004), p. 137.
- [2] H.-M. Kim, *J. Ceram. Soc. Japan*, **109**, S49-S57 (2001).
- [3] T. Kokubo, H.-M. Kim and M. Kawashita, *Biomaterials*, **24**, 2161-2175 (2003).
- [4] H.-M. Kim, F. Miyaji, T. Kokubo and T. Nakamura, *J. Biomed. Mater. Res.*, **32**, 409-417 (1996).
- [5] C. Ohtsuki, H. Iida, S. Hayakawa and A. Osaka, *J. Biomed. Mater. Res.*, **35**, 39-47 (1997).
- [6] M. Nakagawa, L. Zhang, K. Udoh, S. Matsuya and K. Ishikawa, *J. Mater. Sci. Mater. Med.*, **16**, 985-991 (2005).
- [7] T. Kokubo and H. Takadama, *Biomaterials*, **27**, 2907-2915 (2006).
- [8] Y. Matsumoto, Y. Ishikawa, M. Nishida and S. Ii, *J. Phys. Chem. B*, **104**, 4204-4209 (2000).
- [9] A. Sugino, K. Uetsuki, K. Tsuru, S. Hayakawa, A. Osaka and C. Ohtsuki, *Mater. Trans.*, **49**, 428-434 (2008).

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