Micro-pore Formation on Ti-35Nb-xTa Alloy Surface via Plasma Electrolytic Oxidation

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1. INTRODUCTION

- CP-Ti and Ti-6Al-4V alloy have been used for dental and orthopaedic implants due to their physical and mechanical properties such as excellent tensile strength, good corrosion, and wear resistance. However, CP-Ti and Ti-6Al-4V alloys can't naturally form sufficient osteosynthesis with bone tissue due to their biological inertness. Also, the stress shielding effect due to the difference in modulus of elasticity between the implant and the cortical bone causes bone resorption around the cortical bone after implantation, which finally leads to the failure of the implant surgery. In addition, implants made of Ti-6Al-4V alloy, which are generally used, have a problem due to elution of vanadium and aluminum ions when used for a long time in a physiological environment. Vanadium ions are cytotoxic and have carcinogenic properties, and aluminum ions have neurotoxicity, which can affect behavior or neurological function and cause disorders or Alzheimer's disease. In order to solve this problem, many pre-researches have conducted to develop β- type Ti alloys prepared by adding non-toxic and β-type stabilizing elements such as Hf, Nb, Ta, and Nb elements. Particularly, Ta and Nb, when alloyed with Ti, can reduce the modulus of elasticity and promote the improvement of cell adhesion. Plasma electrolytic oxidation (PEO) offers the advantages of quick coating time and controlled coating conditions. The anodized oxide layer and adaptation to a diameter range of Ti alloys promote improvement of cell adhesion.

- In this study, micro-pore formation on Ti-35Nb-xTa alloy surface via plasma electrolytic oxidation was studied using various instruments.

2. MATERIALS AND METHOD

- Ti-35Nb-xTa (x = 0, 3, 7, 15 wt.%) alloys were fabricated using a vacuum arc melting furnace. Thereafter, the sample was heat-treated at 1050 ℃ for 1 hour in an Ar gas atmosphere and water-cooled at 0 ℃ to ensure homogenization.

- Polishing was performed using SiC sandpaper, polishing from 100 to 2000 grit, and finally polishing using alumina powder (3 μm size). The polished samples were ultrasonically washed in ethanol and dried in air, and all the samples were observed by optical microscopy after an etching in solution consisting of 2 mL HF, 3 mL HCl, 5 mL HNO_3, and 190 mL H_2O.

- To examine the effects of Ta contents on the properties of micro-pore, Ti alloys were used as the anode, and the carbone rod as the cathode in the electrolyte containing Ca and P ion for PEO-treatment. For coating, pulsed DC power was used for the power, and the applied voltage and the treatment time were selected to be 3 min at 280 V.

- The surface morphology was observed using OM, FE-SEM, EDS and XRD.

3. RESULTS & DISCUSSION

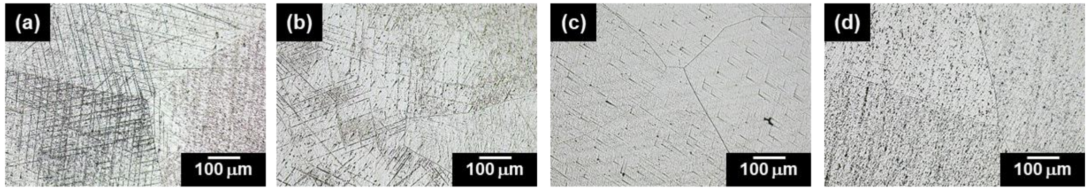

Figure 1. Optical microstructures of Ti-35Nb-xTa alloys after etching; (a) Ti-35Nb; (b) (a) Ti-35Nb-3Ta; (c) Ti-35Nb-7Ta; (d) Ti-35Nb-15Ta.

Table 1. XRF results of Ti-35Nb-xTa

Element	Ti-35Nb	Ti-35Nb-3Ta	Ti-35Nb-7Ta	Ti-35Nb-15Ta
Ti	64.50 ± 0.96	62.29 ± 0.61	58.17 ± 0.93	50.57 ± 0.69
Nb	35.50 ± 0.96	35.45 ± 0.57	35.01 ± 0.78	35.21 ± 0.50
Ta	0	2.26 ± 0.14	6.83 ± 0.33	14.22 ± 0.32

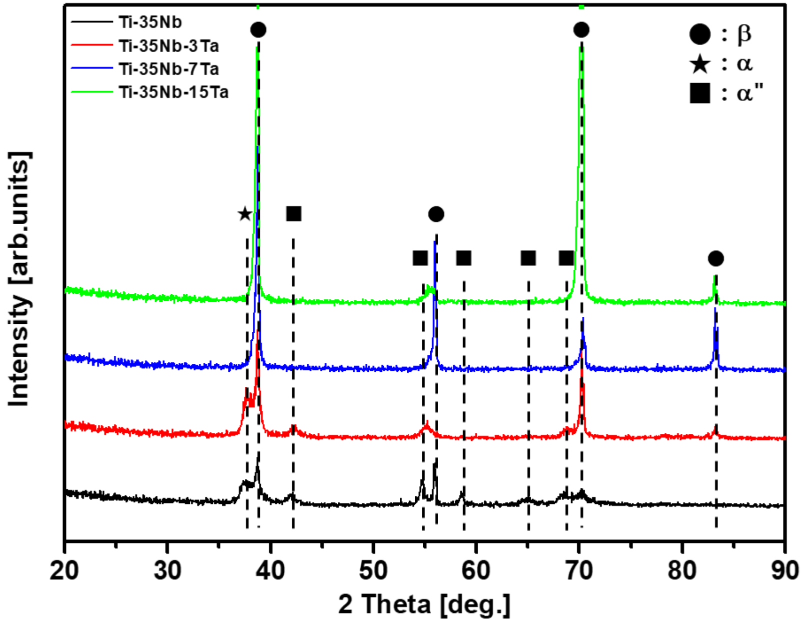

Figure 2. XRD pattern of Ti-35Nb-xTa.

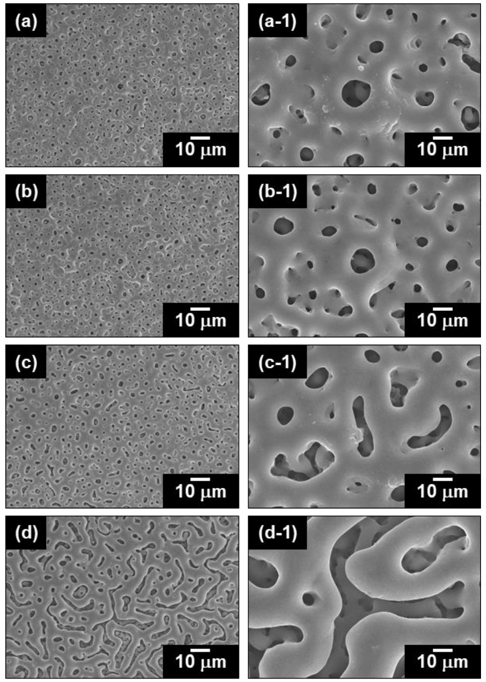

Figure 3. FE-SEM image of Ti-35Nb-xTa alloys after PEO-treatment: (a, a-1) Ti-35Nb, (b, b-1) Ti-35Nb-3Ta, (c, c-1)Ti-35Nb-7Ta, and (d, d-1) Ti-35Nb-15Ta .

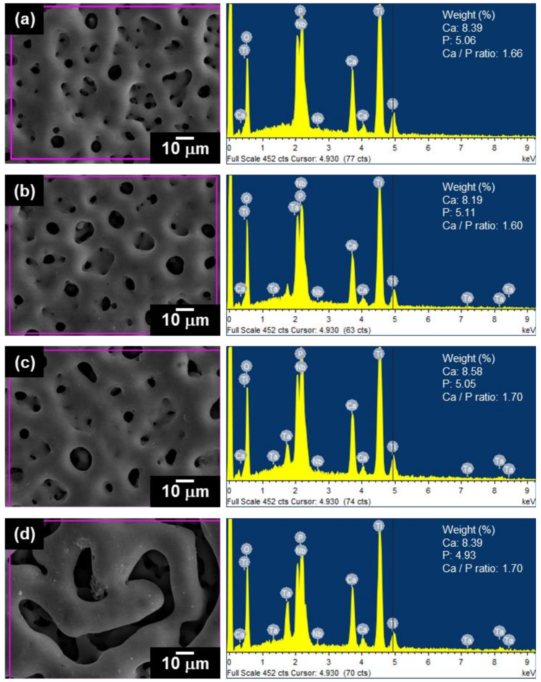

Figure 4. EDS result of Ti-35Nb-xTa alloys after PEO-treatment: (a) Ti-35Nb, (b) Ti-35Nb-3Ta, (c)Ti-35Nb-7Ta, and (d) Ti-35Nb-15Ta .

Table 2. Pore analysis for Ti-35Nb-xTa alloy after PEO-treatment.

Specimen	Ti-35Nb	Ti-35Nb-3Ta	Ti-35Nb-7Ta	Ti-35Nb-15Ta
Porosity (%)	7.25 ± 0.16	10.39 ± 0.04	12.01 ± 0.91	25.65 ± 1.16
Large pore size(㎛)	1.86 ± 0.40	1.90 ± 0.62	2.24 ± 0.65	2.83 ± 1.15
Small pore size(㎛)	0.48 ± 0.13	0.63 ± 0.17	0.77 ± 0.14	-
Number of pore ($25㎛^2$)	66.80 ± 5.53	55.00 ± 4.34	40.40 ± 5.31	12.00 ± 1.90
Fraction of large pores per $25㎛^2$ (%)	27.32 ± 6.11	48.40 ± 3.31	61.14 ± 3.87	90.00 ± 8.43

3. RESULTS & DISCUSSION

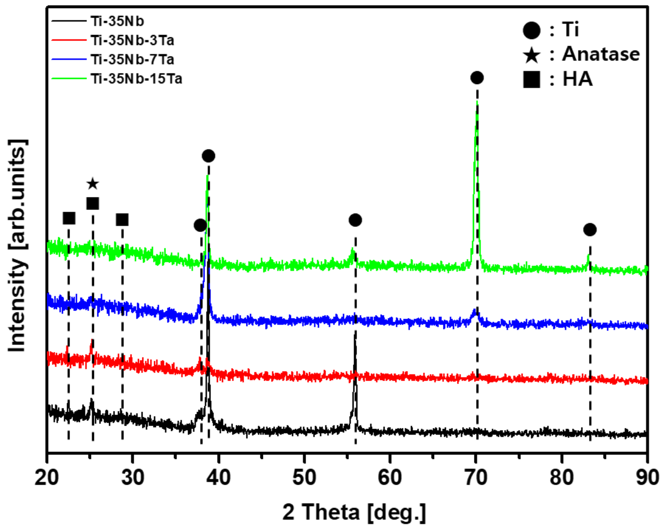

Figure 5. XRD pattern of Ti-35Nb-xTa alloys after PEO-treatment.

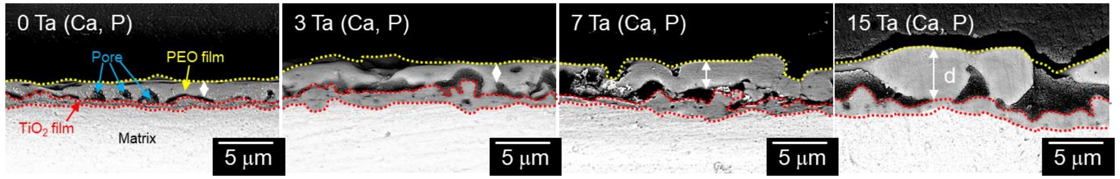

Figure 6. FE-SEM image of cross-sectioned Ti-35Nb-xTa alloys after PEO-treatment.

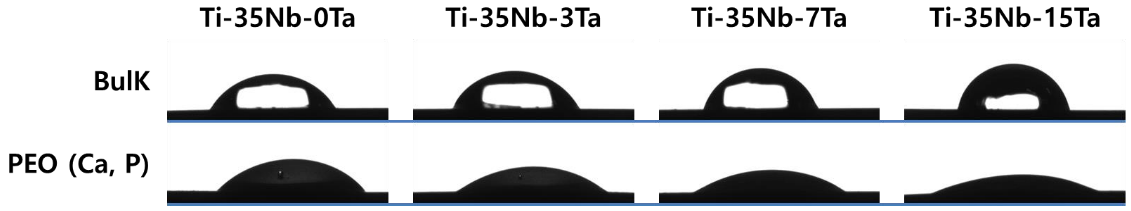

Figure 7. Contact angles of the Ti-35Nb-xTa alloy surfaces.

Table 3. Sectional thickness of Ti-35Nb-xTa alloy after PEO treatment.

Thickness (μm)	0Ta	3Ta	7Ta	15Ta
Ca, P	3.08 ± 0.57	3.93 ± 0.48	4.61 ± 0.37	5.85 ± 0.50

Table 4. Contact angles of the Ti-35Nb-xTa alloy.

Specimen / Contact angle(°)	Ti-35Nb	Ti-35Nb-3Ta	Ti-35Nb-7Ta	Ti-35Nb-15Ta
Etched surface	54.67 ± 2.25	59.29 ± 0.84	67.42 ± 1.11	72.57 ± 1.86
PEO (Ca, P)	44.27 ± 1.26	38.75 ± 0.88	31.58 ± 1.95	21.63 ± 1.06

4. CONCLUSIONS

- Ti-35Nb-xTa alloys were prepared using arc melting machine, and micro-pore was formed on Ti-35Nb-xTa alloys by PEO-treatment.
- As the Ta content increased, the microstructure changed from the needle structure to the equiaxed structure, and changed the α-phase to the β-phase.
- The micropores formed by the PEO treatment showed different shapes depending on the Ta content. As the content of Ta increased, the porosity increased, the size of the pores overall increased, and the number of pores and small pores decreased, and the number of large pores increased. In addition, in the 15Ta alloy, groove shaped pores appeared.
- The XRD peaks of α, α”, and β were detected for Ti-35Nb-xTa alloy, and after PEO-treatment the XRD peaks of anatase and hydroxiapatite was detected.
- Ca and P ions were detected on the micro-pore surface, and the Ca/P ratio was similar to the stoichiometric ratio.
- As the Ta content increased, the thickness of the oxide film increased from 3.08 to 5.85 μm, and the contact angle decreased after PEO treatment compared to before PEO treatment, and the contact angle decreased as Ta content increased.
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