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Corrosion Characteristics of Cell-Covered Ternary Ti-Nb-Ta Alloy for Biomaterials

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Ti and Ti-alloys have good biocompatibility, appropriate mechanical properties and excellent corrosion resistance. However, the widely used Ti-6Al-4V is found to release toxic ions (Al and V) into the body, leading to undesirable long-term effects. Ti-6Al-4V has much higher elastic modulus (100 GPa) than cortical bone (20 GPa). Therefore, titanium alloys with low elastic modulus have been developed as biomaterials to minimize stress shielding. The electrochemical behavior of surface-modified and MC3T3-E1 cell-cultured Ti-30(Nb,Ta) alloys with low elastic modulus have been investigated using various electrochemical methods. Surfaces of test samples were treated as follows: 0.3 μm polished; 25 μm, 50 μm and 125 μm sandblasted. Specimen surfaces were cultured with MC3T3-E1 cells for 2 days. Average surface roughness (R_a) and morphology of specimens were determined using a surface profilometer, OM, and FE-SEM. Corrosion behavior was investigated using a potentiostat(EG&G PARSTAT 2273), and electrochemical impedance spectroscopy was performed (10 mHz to 100 kHz) in 0.9% NaCl solution at 36.5 ± 1 ℃. The microstructures of the Ti-30(Ta,Nb) alloys had a needle-like appearance. The R_a of polished Ti-30Ta and Ti-30Nb alloys was lower than that of the sandblasted Ti alloy. Cultured cells displayed round shapes. For polished alloy samples, cells were well-cultured on all surfaces compared to sandblasted alloy samples. In sandblasted and cell-cultured Ti-30(Nb,Ta) alloy, the pitting potential decreased and passive current density increased as R_a increased. Anodic polarization curves of cell-cultured Ti alloys showed unstable behavior in the passive region compared to non-cell-cultured alloys. From impedance tests of sandblasted and cell-cultured alloys, the polarization resistance decreased as R_a increased, whereas, R_a for cell-cultured Ti alloys increased compared to non-cell-cultured Ti alloys.

Keywords *: corrosion behavior, Ti-Nb-Ta alloy, dental materials, polarization resistance.*

1. Introduction

Recently, Ti-Nb and Ti-Ta based alloy systems have been studied and found to display both lower elastic moduli and higher tensile strengths than are common for metals and alloys. Nb, and Ta can be stabilized to β-phase of Ti alloy and β-phase structure exhibits about 60-80 GPa of Young's modulus.[1)] Some researcher reported that the Ti-30%Ta alloy with martensite α"-phase has the potential to become a new candidate for biomedical application due to its good combination of low modulus and high strength. To improve bone tissue integration on implant surfaces, various techniques have been used to increase the roughness of the implant surfaces.[2)] Cell adhesion and proliferation depend on surface roughness[3)] and metal ion dissolution.[4)] That is, cell adhesion is a very specific parameter and describes the relative adherence of a cell to its substrate, generally at an early stage of culture when the cells are directly in contact with the material surface.[3)] Metal ion released from metallic materials implanted into human body is usually accelerated by chemical species in the body. Metal ion dissolution is inhibited by the surface oxide as a passive film,[4)] whereas toxicity elements act inhibitors against the cell adhesion and proliferation. In this study, titanium alloys with low elastic modulus have been developed as biomaterials to minimize stress shielding. The electrochemical behavior of surface-modified and MC3T3-E1 cell-cultured Ti-30(Nb,Ta) alloys with low elastic modulus have been investigated using various electrochemical methods.

2.1 Alloy preparation

Ti-Ta-Nb alloys were prepared by using high purity sponge Ti (G&S TITANIUM, Grade. 4, USA), Ta and

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Nb sphere (Kurt J. Lesker Company, 99.95% wt.% in purity). Two kinds of Ti alloys prepared using the vacuum arc melting furnace. The weighed charge materials were prepared by the vacuum arc furnace, flowing the purified Ar gas into water cooling copper hearth chamber in vacuum atmosphere of 10^{-3}torr, and controlled atmosphere in chamber by method to keep vacuum again. Also, before melting, the constituents were cleaned with methanol to minimize oxygen quantity and surface contaminants in chamber and pure Ti was melted six times with purified argon gas. After that, melting treatment was carried out more than six times by reversing the alloy sponges in order to homogenize, and each time was held in the molted state for 5 min. in a high purity argon atmosphere by arc furnace with water-cooled copper hearth and solution treatment was carried out for 6hrs at 1000 ℃ in Ar gas atmosphere.

2.2 Surface treatment and cell culture

Surfaces of test samples were treated as follows: 0.3 µm polished; 25 µm, 50 µm and 125 µm sandblasted. Specimen surfaces were cultured with MC3T3-E1 cells for 2 days. Average surface roughness (R_a) and morphology of specimens were determined using a surface profilometer, OM, and FE-SEM.

2.3 Corrosion test

The electrochemical behavior of surface-modified and MC3T3-E1 cell-cultured Ti-30(Nb,Ta) alloys with low elastic modulus have been investigated using various electrochemical methods. Corrosion behavior was investigated using a potentiostat(EG&G PARSTAT 2273), and electrochemical impedance spectroscopy was performed (10 mHz to 100 kHz) in 0.9% NaCl solution at 36.5±1℃ at scan rate of 1.67 ㎷/sec. Electrochemical impedance spectroscopy was performed (10 mHz to 100 kHz) in 0.9% NaCl solution at 36.5±1 ℃. All electrochemical characteristics were performed in a standard three-electrode cell having specimen as a working electrode and a high carbon as counter electrode. The potential of working electrode was measured against a saturated calomel electrode (SCE) and all given potentials were referred to this electrode. After electrochemical corrosion tests, the surfaces of each specimen were investigated by using FE-SEM.

3. Results and discussion

Fig. 1 is OM and SEM micrographs showing the microstructure of homogenized Ti alloy surface. Fig. 1(a) and (c) show the microstructure of Ti-30Nb alloy. Fig. 1(b)

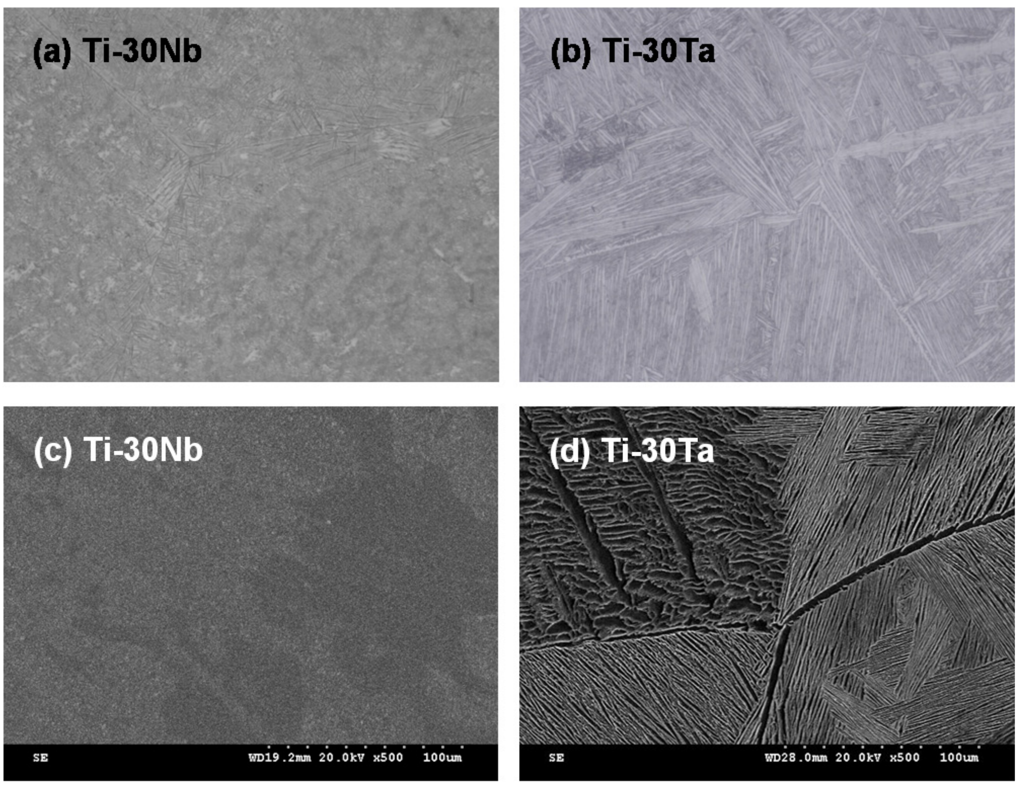

Fig. 1. OM and SEM micrographs showing the microstructure of homogenized Ti-30Nb(a,c) and Ti-30Ta(b,d) alloy surface(X 500). (a),(b) OM (c),(d) SEM.

and (d) show the microstructure of Ti-30Ta alloy, respectively. The microstructures of the Ti-30(Ta,Nb) alloys had a needle-like appearance. It is consistent with pre-researched results[5),6)] that the quenched alloys exhibit lamellar martensite α' structure at a Ta content below 20 wt%, needle-like orthorhombic martensite α" structure at a Ta content from 30 to 50 wt%. These photos show the two phases, α and β-phase, and it is estimated that the white part was α phase and black part was β-phase. The α-phase, white image in figure, decreases as the amount of Ti and Nb increases.[6)] We confirmed that the microstructure changes from α phase to β-phase through XRD and β phase increases according to the amount of Nb added.[6)] With these results, we could make an analogical inference that Nb and Ta is the β stabilizing element as the β-phase increases according to the addition of Nb and Ta.

Fig. 2 shows SEM micrographs of the non-cell cultured

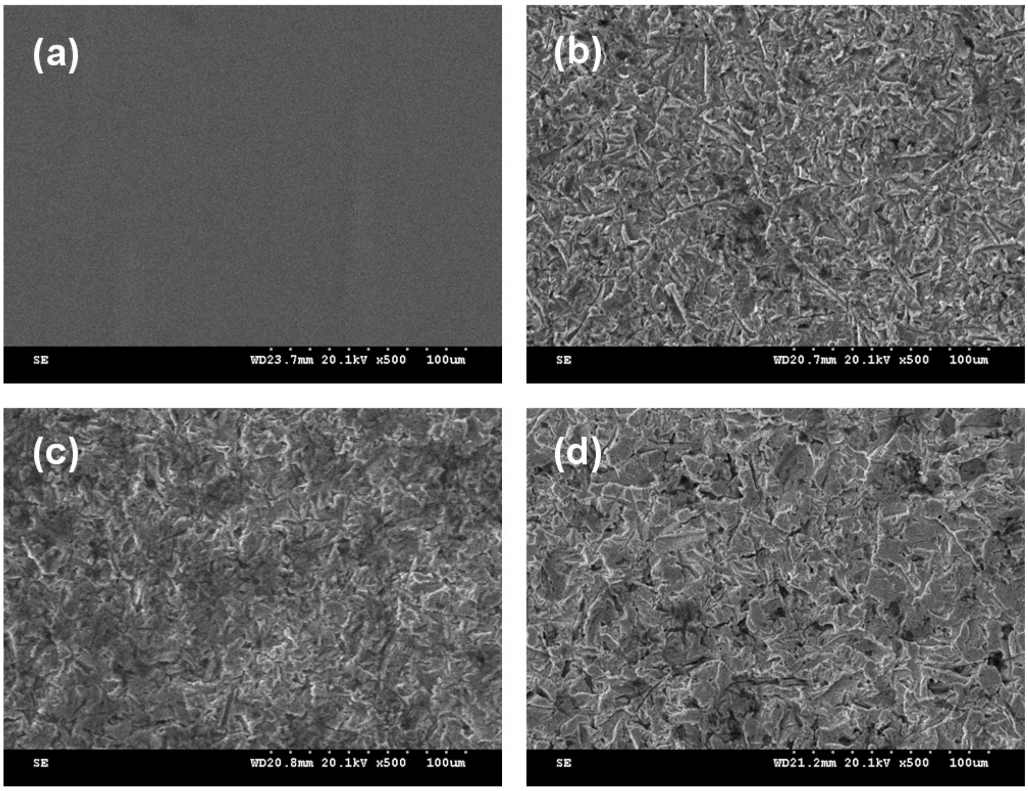

Fig. 2. SEM micrographs showing the non-cell cultured Ti-30Ta surface. (a) polished (b) 25㎛ sandblasted (c) 50㎛ sandblasted (d) 125㎛ sandblasted.

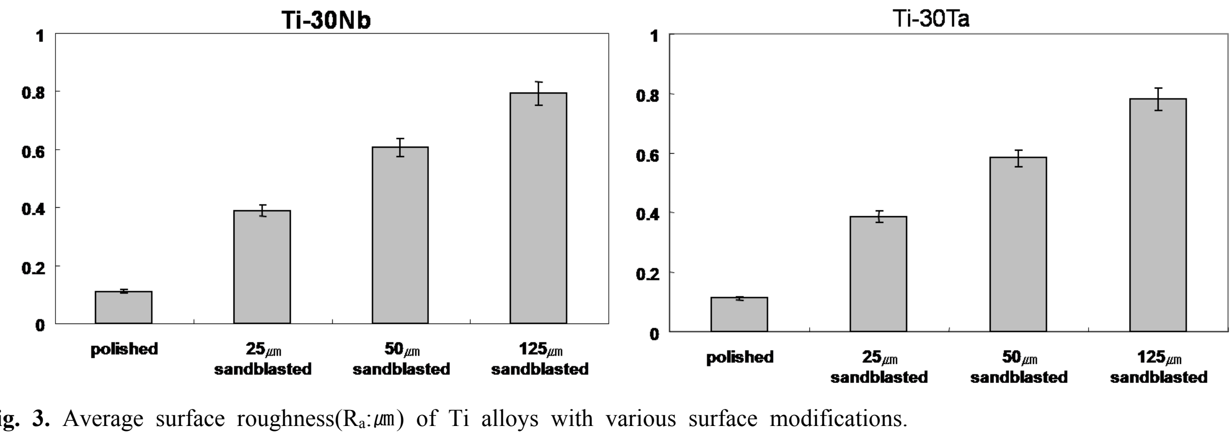

Fig. 3. Average surface roughness(R_a:㎛) of Ti alloys with various surface modifications.

Ti-30Ta surface. Fig. 2 (a) is polished, (b) is 25㎛ sandblasted, (c) is 50㎛ sandblasted, and (d) is 125㎛ sandblasted surface of samples. It is confirmed that the surface roughness increased as size of aluminum oxide particle increased. The R_a of polished Ti-30Ta and Ti-30Nb alloys was lower than that of the sandblasted Ti alloy from Fig. 3.

Fig. 4 shows SEM micrographs of MC3T3-E1 cell cultured on Ti-30 Ta surface. Fig. 4(a) is polished, (b) is 25㎛ sandblasted, (c) is 50㎛ sandblasted, and (d) is 125㎛ sandblasted specimen surface. On polished and 25㎛ sandblasted surface, the cell were more widely spread with lamellipods[7] demonstrating cell migration and no particular orientation of cells was observed. Cell growth and size increased and more cytoplasmic prolongations were observed at rough surfaces. Cultured cells displayed round shapes. Cells were well-cultured on the polished surfaces compared to sandblasted alloy samples.

Fig. 5 shows the potentiodynamic polarization curves

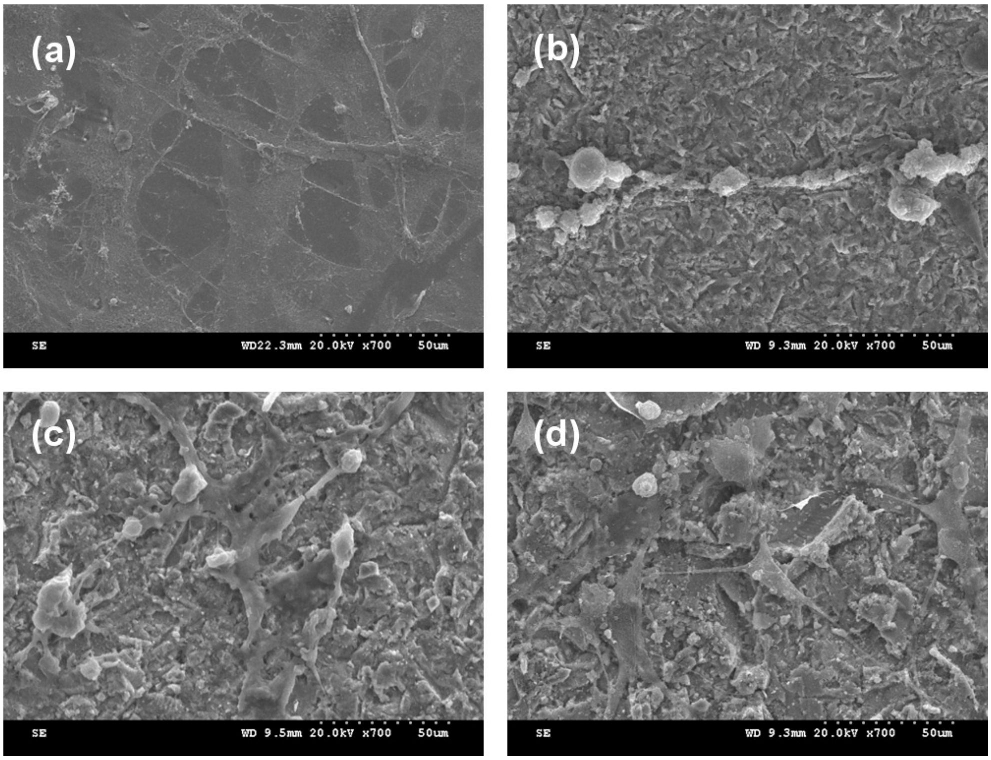

Fig. 4. SEM micrographs showing MC3T3-E1 cell cultured on Ti-30 Ta surface. (a) polished (b) 25㎛ sandblasted (c) 50㎛ sandblasted (d) 125㎛ sandblasted.

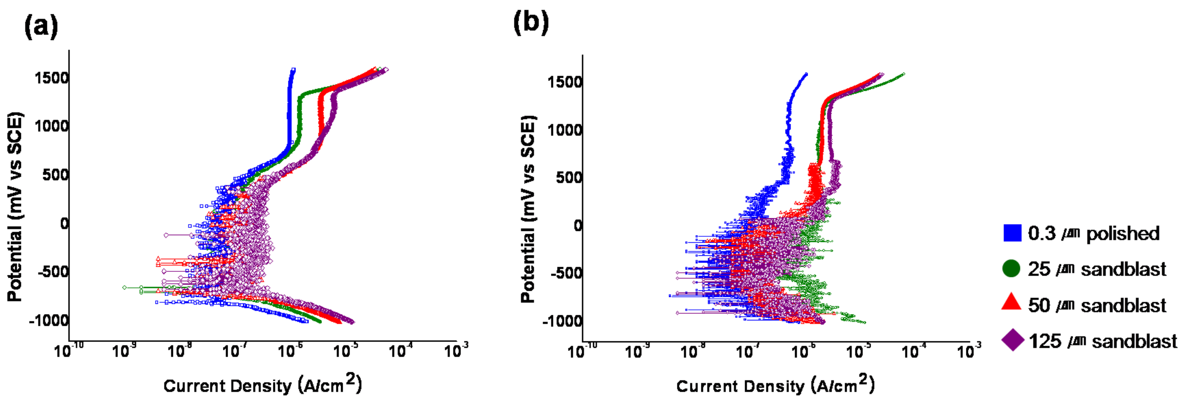

Fig. 5. Potentiodynamic polarization curves of MC3T3-E1 cell cultured Ti alloys after potentiodynamic test in 0.9% NaCl solution at 36.5 ± 1℃. (a) Ti-30Nb (b) Ti-30Ta.

of cell cultured Ti-30Nb(a) and Ti-30Ta(b) alloys after potentiodynamic test in 0.9% NaCl solution at 36.5 ± 1℃. It could see that the corrosion potentials(E_{corr}) of Ti-30Nb and Ti-30Ta show similar potential(-400~-500 mV), but current density in passive region largely decreased as R_a increased. It is confirmed that the pit formed by aluminum oxide particles increased on the surface and this pit caused site to be more susceptible to aggressive ion like Cl^-.[2)] Whereas polished surface shows a stable passive region in anodic polarization curves because Ti combines with oxygen and forms a stable immunity such as the TiO_2 film on the surface. Anodic polarization curves of cell-cultured Ti alloys showed unstable behavior in the passive region compared to non-cell-cultured alloys.

In sandblasted Ti-30(Nb,Ta) alloy, the pitting potential(E_{pit}) decreased and passive current density(I_{pass}) of cell-cultured Ti-30(Nb,Ta) alloy increased as R_a increased because covered cell on the surface has better corrosion resistance than non-cell cultured Ti alloy. It is assumed that the cell plays a role to improve the corrosion resistance like passive film and it prohibits the active corrosion site formed by sandblasting treatment. The presence of cells on Ti-30(Nb,Ta) alloy alloy leads to an increase in passivation of metals. In case the Ti-30Nb alloy, E_{pit} is higher than that of Ti-30Ta alloy.

Fig. 6 and 7 show Nyquist plot of non-cell and cell cultured Ti-30Nb(a) and Ti-30Ta(b) alloys after AC impedance test in 0.9% NaCl solution at 36.5 ± 1℃. The polarization resistance(R_p)of non-cell cultured alloy is lower than that of cell cultured alloy. From impedance tests of sandblasted and cell-cultured alloys, the polarization resistance decreased as R_a increased, whereas, R_a for cell-cultured Ti alloys increased compared to non-cell-cultured Ti alloys. The high value of R_p implies a high corrosion resistance of alloy, that is, a low rate of released metallic ion into the electrolytic solution or cell on the surface. The Bode plot results indicated that the corrosion behavior of alloy in solution was under charge-transfer controlled because of the local variation of aggressive ion like Cl^-, preferentially attacking or damaging the oxide film and

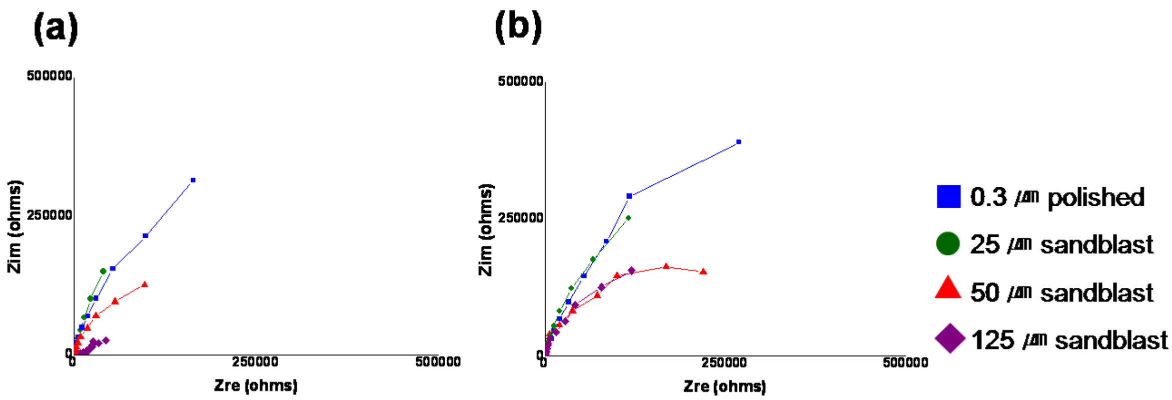

Fig. 6. Nyquist plot of non-cell cultured Ti alloys after AC impedance test in 0.9% NaCl solution at 36.5±1℃. (a) Ti-30Nb (b) Ti-30Ta.

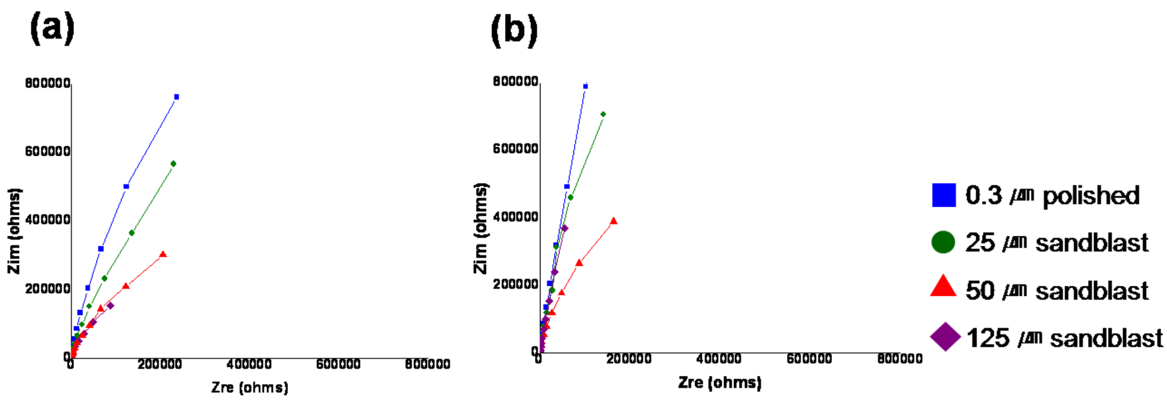

Fig. 7. Nyquist plot of MC3T3-E1 cell cultured Ti alloys after AC impedance test in 0.9% NaCl solution at 36.5±1℃. (a) Ti-30Nb (b) Ti-30Ta.

covered cell. The Bode plots for all the alloys showed near capacitive response in the lower and middle frequency region which was characterized by slope≈-1 in the log|z| vs. log(f) curve.[8] It can also be observed that the |z| values in high frequency region increased as R_a decreased and cell proliferation increased. In conclusion, the R_p of Ti and Ti-6Al-4V alloy cultured with cells increases with the cell growth, including adhesion, spreading, and proliferation.

4. Conclusions

The microstructures of the Ti-30(Ta,Nb) alloys had a needle-like appearance. The R_a of polished Ti-30Ta and Ti-30Nb alloys was lower than that of the sandblasted Ti alloy. Cultured cells displayed round shapes. For polished alloy samples, cells were well-cultured on all surfaces compared to sandblasted alloy samples. In sandblasted and cell-cultured Ti-30(Nb,Ta) alloy, the pitting potential decreased and passive current density increased as R_a increased. Anodic polarization curves of cell-cultured Ti alloys showed unstable behavior in the passive region compared to non-cell-cultured alloys. From impedance tests of sandblasted and cell-cultured alloys, the polarization resistance decreased as R_a increased, whereas, R_a for cell-cultured Ti alloys increased compared to non-cell-cultured Ti alloys.

References

1. D. Kuroda and M. Niiomi, *Materials Sci and Eng A*, **243**, 244 (2001).
2. H. C. Choe and Y.M. Ko, *Materials Science Forum*, **475**, 2287 (2005).
3. K. Anselme, *Biomaterials*. **21**, 667 (2000).
4. T. Hanawa, *Matr. Sci. & Eng*. **24**, 745 (2004).
5. Y. L. Zhou, M. Niinomi, and T. Akahori. *Matr. Sci. & Eng A*, **371**, 283 (2004).
6. J. J. Park, H. C. Choe, and Y.M. Ko. *Materials Science Forum*, **539**, 1270 (2007).
7. K. Anselme, P. Linez, M. Bigerelle, D. Le Maguer, A. Le Maguer, P. Hardouin, H. F. Hilderbrand, A. Iost, and J. M. Leroy. *Biomaterials*, **21**, 1567 (2000).
8. N. Ibris and JCM. Rosca, *J. Electroanalytical Chemistry*, **526**, 53 (2002).