

Anodic Dissolution of Ti in EMIC-AlCl₃ Ionic Liquid or LiCl-KCl Molten Salt for Enhancement of Adhesion Between Bone Cell and Ti Substrate

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For application of Ti to the bio-implant materials, the anodic etching of Ti in the molten salt of LiCl-KCl and EMIC-AlCl₃ was investigated. The roughness of the Ti surface after the etching was examined from the SEM observation. The etching of the Ti electrode in the melt of LiCl-KCl did not form a suitably rough surface morphology. In the melt, the largely rough surface was formed with top-to-bottom distance of 10 μm. The etching in the melt of EMIC-AlCl₃ at the potential of 0.6 V vs. Al/Al(III) introduced the formation of a rough surface applicable to the Ti implant. The rough surface formed in the melt exhibits the top-to bottom distance of about 1 μm.

Key words: Ti, molten salt, ionic liquid, EMIC-AlCl₃, anodic dissolution

INTRODUCTION

Titanium and its alloys are used as substitutional material for bone and tooth root^[1]. However, they do not have so high bioactivity that the following surface modification have been proposed for the enhancement of the osteoconductivity; (i) coating of bioactive materials on the implant, such as hydroxyapatite-based compound^[2], TiO₂^[3], CaTiO₃^[4], and their composite coatings^[5], and (ii) construction of surface topography such as screw and 3D porous structure^[6]. On the surface topography, about 200 μm pores in diameter have been proposed to be suitable to on the implant surface to initiate the fixation (the anchor effect) due to the growth of the new bone into the pores. In addition, the surface roughness in sub μm or μm level was reported to influence the osteoconductivity. R. G. Flemming et al. reviewed that the cell culturing depended on the surface roughness produced by the lithographic technique^[7]. We previously

found that a combination between the surface roughness in the μm level and TiO₂ coating revealed a large benefit to the osteoconductivity, which was evaluated under the in vivo condition^[8].

It may be not easy to control the surface geometric patterns at the μm level or less on the titanium implants with complicated shape by mechanical machining, and also by chemical treatments.

In this paper, we report the anodic etching of Ti in the EMIC-AlCl₃ and LiCl-KCl molten salts for the formation of the rough surface at the μm level on the titanium for the application of the implant. Further we examine the conditions for the formation of a suitable rough surface to the Ti implant.

EXPERIMENTAL

Lithium chloride (LiCl, Wako, 99.5 % pure), potassium chloride (KCl, Wako, 99.5 % pure), and

1-ethyl-3-methyl-imidazolium chloride (EMIC, Aldrich, 99% pure) were used as received. Aluminum chloride (Aldrich, 99.9% pure) was sublimed and condensed before use. Illustration of electrochemical cell for anodic dissolution of Ti is shown in Fig. 1. The cell was made from a Pyrex glass vessel and equipped with a heater around the outside. The LiCl-KCl molten salt was melted at 673K. The cell was filled with Ar. The AlCl₃-EMIC melt preparation and anodic dissolution was carried out in an Ar-filled glove box (H₂O level < 7 ppm). A 100 g AlCl₃-EMIC (molar ratio of 2 : 1) salt sample was melted at 298 K and was purified by high purity aluminum wire (Kojundo chemical lab, 99.999%).

Titanium plates (Johnson Matthey, 99.5%) were used as a working electrode and as a counter electrode, respectively. A pure aluminum wire (Nilaco, 99.99%) placed in a small Pyrex glass tube filled with the AlCl₃-EMIC (2 : 1) melt was used as a reference electrode in AlCl₃-EMIC melt. An Ag wire (Nilaco, 99.9%) placed in the mulite tube filled with LiCl-KCl-AgCl melt was used as a reference electrode in LiCl-KCl molten salt at 673 K. Potential difference between Ag/Ag⁺ and Al/Al(III) is about 0.7 V in AlCl₃-EMIC molten salt. To maintain electrical contact between the electrolyte melt and the reference electrode, a small hole was made by insertion of ceramic fiber at the bottom of the tube. Voltammogram was recorded at a potential region from -0.2 to 1.5 V vs. Al/Al(III) with a scan rate of 0.1 V/s in the AlCl₃-EMIC molten salt. Anodic dissolution of Ti was carried out with 25 or 50 C/cm² electric charges by a Hokuto-Denko HAG-5010 potentiostat.

The surface observation of the specimen was used by scanning electron microscopy (SEM, JEOL JXA-8900M).

RESULTS AND DISCUSSION

LiCl-KCl molten salt

The anodic voltammogram of the Ti electrode in the melt of LiCl-KCl is shown in Fig. 2, where the potential sweep was made from -1.3 V to 0.0 V vs. Ag/Ag⁺ at a rate of 0.1 V/s in the anodic direction. The voltammogram reveals an active-passive transition. The current density (CD) increases with increase of the potential to 0.8 A/cm² at

-0.85 V and then suddenly decreases at -0.8 V. The CD remains almost constant at 0.2 A/cm² in the potentials higher than -0.8 V. The equilibrium potentials of Ti oxidation in the LiCl-KCl melt were reported to be -1.0 V and -0.61 V for Ti/Ti(II) and Ti(II)/Ti(III), respectively.⁹⁾ The active dissolution to -0.75 V may be a dissolution of Ti metal to Ti(II). In the potentials higher than -0.8 V, a salt layer of Ti(III) or Ti(IV) may be formed, restricting the dissolution of Ti.

We selected three etching potentials to obtain the rough and bio-active surface, i.e., -1.1, -0.7, and 0.0 V. The electrolysis was made with 50 C/cm² electric charge at the individual potentials and the surface morphology was observed by SEM. The SEM view of the surface is shown in Fig. 3. At 0.0 V at which the dissolution may be restricted by the formation of a salt layer, the surface exhibits relatively smooth and homogeneous. The rougher surface was observed at potentials of -1.1 V and -0.7 V. A morphology having small dimples are seen at -0.7 V. Another morphology consisting of small crystal faces or grains is found at -1.1 V. The peak-to-bottom distance at the rough surface after the electrolysis at -1.1 V was about 3 μm.

The roughness of the surface is changed with the electric charge applied. The change is shown in Fig. 4. The up-and-down of the surface may depend on the crystal orientation of the grains due to the difference in the dissolution rate. The roughness estimated from the top-to-bottom distance is increased from 0.54 μm at 10 C/cm² to 11.0 μm at 200 C/cm². Therefore the mm roughness structure, required for the bio-active surface, was obtained using the anodic etching in the melt of LiCl-KCl. However it is difficult to form fine rough structure in LiCl-KCl due to the fast etching rate. Slower etching rate compared with the LiCl-KCl melt gives easy control of the surface roughness.

EMIC-AlCl₃ room temperature molten salt

The anodic voltammogram of the Ti electrode in the melt of EMIC-AlCl₃ is shown in Fig. 5. The anodic CD is seen at the potential higher than 0.3 V vs. Al/Al(III). An active-passive transition is seen on the voltammogram similarly as that in the melt of LiCl-KCl. On the voltammogram, the peak of CD appears at around 0.6 V,

then CD suddenly decreased. The CD remains almost constant at potentials higher than 0.65 V. At the potentials higher than 0.7 V, the color of the molten salt is changed to purple at the neighbor of the Ti electrode. This color may be formation of Ti(III) ions dissolving from the Ti electrode. It is noteworthy that the CD about one tenth smaller than that in the LiCl-KCl.

We selected the potentials of 0.4, 0.5 and 0.6 V and compared the surface morphology after the electrolysis with electric charge of 25 C/cm². The SEM view of the surface is shown in Fig. 6. For the etching at 0.4 V, the surface roughness is small, being relatively smooth. The surface roughness increases with the higher potential. After the etching at 0.6 V, the top-to-bottom distance reaches 1 μm, which may be suitable for application to the implant.

The surface morphology is changed with electric charge at 0.6 V, which is given in Fig. 7. The surface morphology may be not applicable to the implant by electrolysis at the electric charge less than 12.5 C/cm²; however, it reveals a suitable feature after the electrolysis at 25 and 50 C/cm². It is noticeable that the surface morphology does not dramatically change during the electrolysis at the electric charge more than 25 C/cm². Therefore anodic etching in the EMIC-AlCl₃ melt is effective for easy control of μm roughness structure.

CONCLUSION

1. The etching of the Ti electrode in the melt of LiCl-KCl is difficult to form fine rough structure due to fast etching rate.
2. The etching in the melt of EMIC-AlCl₃ at the potential of 0.6 V vs. Al/Al(III) introduces the formation of a rough surface applicable to the Ti implant.

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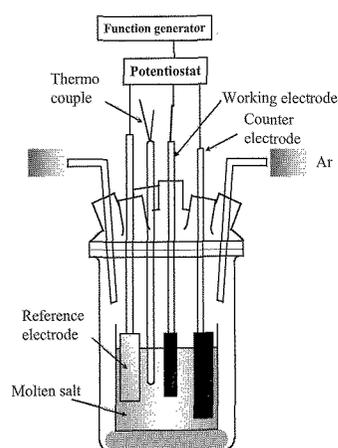


Fig. 1 Schematic illustration of electrochemical cell.

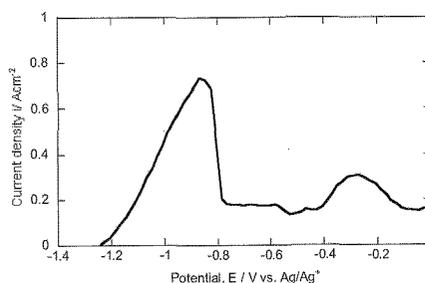


Fig. 2 Anodic voltammogram on Ti in LiCl-KCl molten salt at 673K.

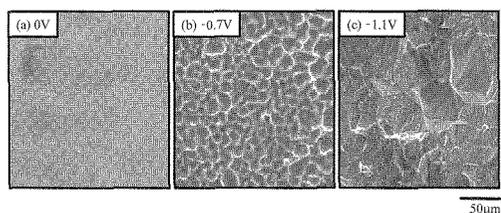
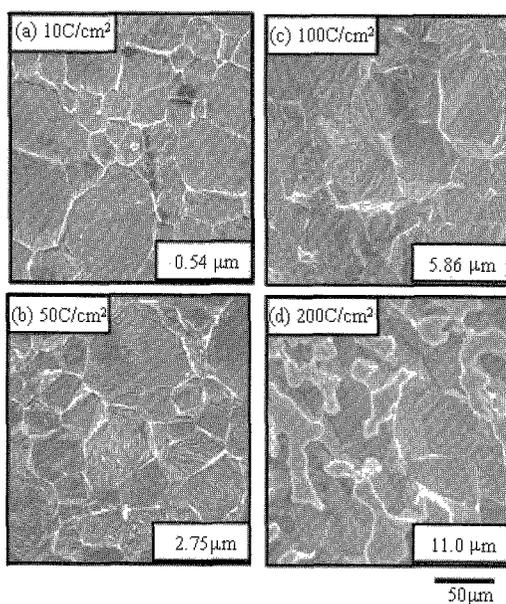


Fig. 3 SEM image of Ti surface after anodic etching in potential at (a) 0V, (b) -0.7V, and (c) -1.1V.

Fig. 4 SEM image of Ti surface after anodic etching at



-1.1V with electric charge of (a)10 C/cm², (b)50 C/cm², (c)100 C/cm², and (d)200 C/cm².

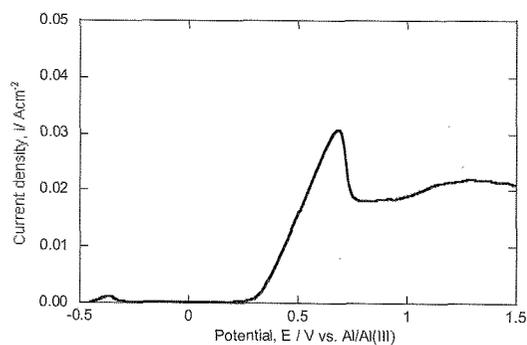


Fig. 5 Anodic voltammogram on Ti in EMIC- AlCl_3 room temperature molten salt at 298K.

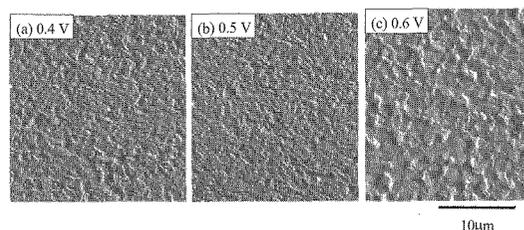


Fig. 6 SEM image of Ti surface after anodic etching at (a) 0.4V, (b) 0.5V, and (c)0.6V with electric charge of 25 C/cm².

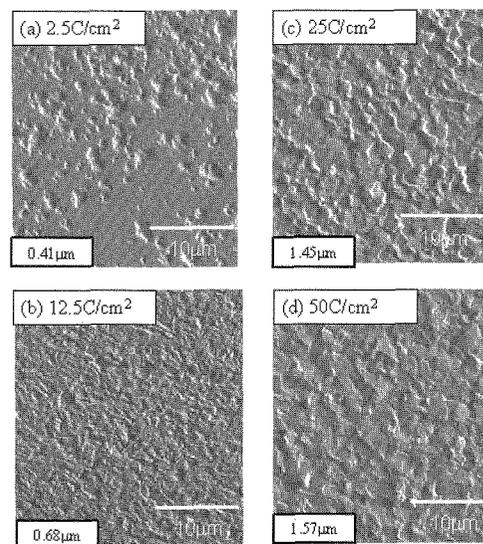


Fig.7 SEM image of Ti surface after anodic etching at 0.6V with electric charge of (a)2.5 C/cm², (b)12.5 C/cm², (c)25 C/cm², and (d)50 C/cm².

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