Immediate soft-tissue adhesive titanium: The effect of surface porosity

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1. Introduction

There is an increasing use of titanium (Ti) implant devices interfacing with non-keratinized soft tissues in modern craniomaxillofacial surgery, and a close attachment of soft tissues onto Ti surface is regarded as an optimal condition for preventing complications, such as infections and abscess formation.

We recently reported that pure Ti or Ti alloy film after an acid treatment and air drying showed a remarkable soft tissue adhesiveness immediately (*i.e.*, within a few seconds; see supplementary information I) after the attachment onto soft tissues, demonstrated by *ex vivo* shear adhesion tests with mouse dermal tissues and by *in vivo* implantation tests in mouse subcutaneous tissues.[1,2]

Herein, we report the effect of surface geometry of moisture-permeable Ti mesh on the immediate soft-tissue adhesion property after the acid treatment.

2. Methods

Perforated Ti mesh films with different hole sizes (25–500 μm) and pitches (50–1,000 μm) were fabricated by laser-ablation or photolithography etching process (Yagishita Giken Co. Ltd., Saitama, Japan) using commercially-pure Ti films (grade 1; 15 μm in thickness; TR2700C-H: Takeuchi Kinzoku-hakuhun Kogyo Co. Ltd., Tokyo, Japan). The aperture ratio was set to 22.7% in this study. The acid treatment of films was conducted with a mixed solution of 45 wt% H_2SO_4 and 15 wt% HCl in water at 70˚C, and the treated films were dried in air at 60˚C for 24 h. The moisture permeability was evaluated by water vapor transmission rate (WVTR) measured from the weight loss of water covered with the films. The soft tissue adhesion properties of the films were evaluated by lap shear adhesion tests using mouse dermal tissues excised from the back of 6-week-old male BALB/c mice (Japan SLC, Inc., Shizuoka, Japan)[1)] in accordance with the Guidelines for Animal Experiments at Okayama University after approval of the experimental protocol by Okayama University (OKU-2020530).

3. Results and Discussion

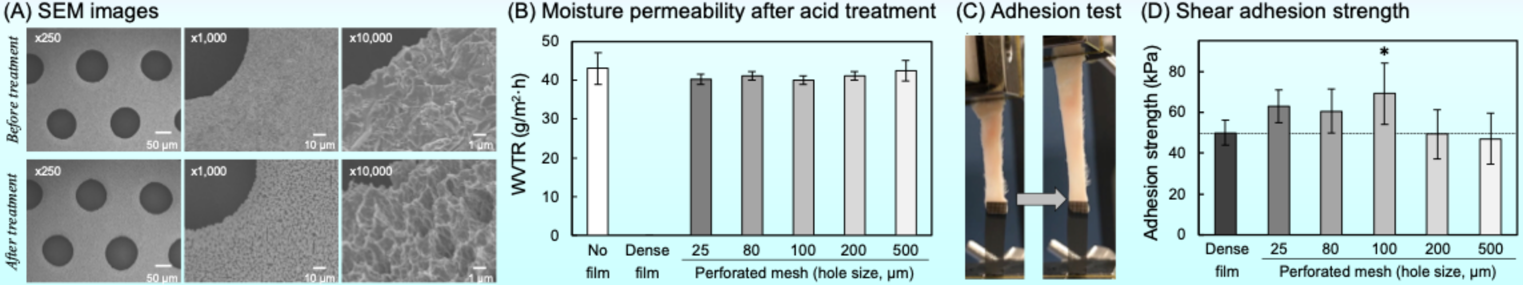

Figure 1. (A) Typical SEM photographs of Ti mesh (pore size, 100 μm; pitch, 200 μm) before and after acid treatment. (B) Moisture permeability of the samples after acid treatments. (C) Digital photographs taken during a shear adhesion test of the Ti mesh with with a mouse dermal tissue. (D) Shear adhesion strengths of dense and perforated Ti films with different pore sizes. Error bars indicate standard deviations (n=5) and the asterisk indicate statistically significant differences with dense Ti film, as determined by a Dunnett test ($p<0.05$).

X-ray diffraction analysis revealed that titanium hydrides (δ-TiHx) were formed on the acid-treated Ti surfaces, and the surface roughness increased by the acid treatment (Fig. 1A). The hole size was not significantly changed after the acid treatment in this study. The WVTR of dense Ti film was almost zero, whereas the WVTR of perforated Ti meshes (aperture ratios, 22.7%) was almost the same as water without any covers (Fig. 1B).

From the lap shear adhesion tests (Fig. 1C), the perforated Ti mesh films also adhered immediately after the attachment onto the dermal tissues. Interestingly, the acid-treated Ti mesh with 100 μm holes showed the largest soft tissue adhesion strength (Fig. 1D). The enhanced adhesion strength would be due to the increased contact area between Ti and soft tissues by the penetration of tissues inside the holes on the meshes.

4. Conclusions

The moisture-permeable Ti meshes after the acid treatment adhered immediately to mouse dermal tissues without decreasing the adhesion strength. The 100 μm sized holes on the acid-treated Ti mesh enhanced the soft tissue adhesion.

5. References

1) Okada M, *et al.* Titanium as an instant adhesive for biological soft tissue. *Adv Mater Interfaces* 2020; **7**: 1902089.
2) Wang Y and Okada M, *et. al.* Immediate soft-tissue adhesion and the mechanical properties of the Ti–6Al–4V alloy after long-term acid treatment. *J Mater Chem B* 2021; **9**: 8348-8354.

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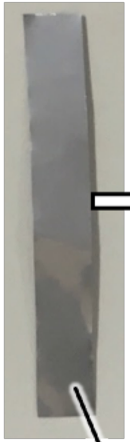
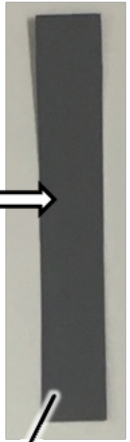
Supplementary information I: Abstract of previous works [*Adv. Mater. Interfaces* **7** (2020) 1902089; *J. Mater. Chem. B* **9** (2021) 8348]

Commercially-pure titanium

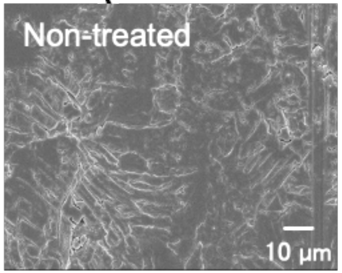


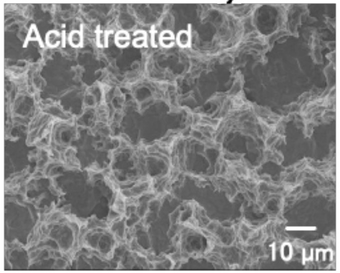
(grade 1; thickness, 15 μm)

Acid treatment with H_2SO_4/HCl



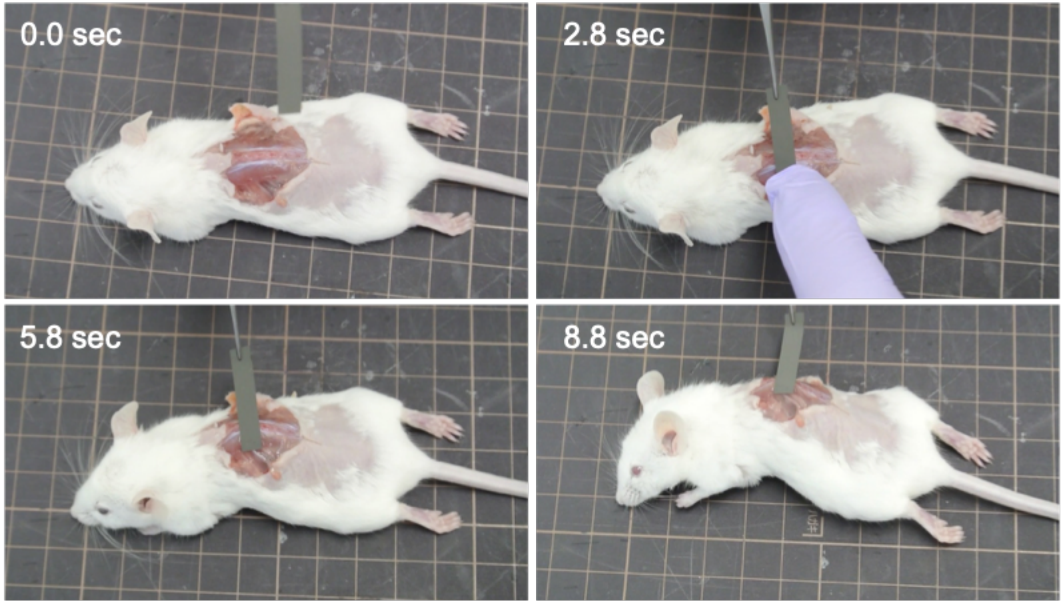
- Etching of Ti
- Formation of δ-TiH_x
- Increased roughness
- Increased hydrophobicity (Water contact angle, 91°)





The acid treated titanium could adhere immediately on soft tissues

https://onlinelibrary.wiley.com/doi/full/10.1002/admi.201902089



Immediate adhesion of the acid-treated titanium film on a mouse fascia (within several seconds)

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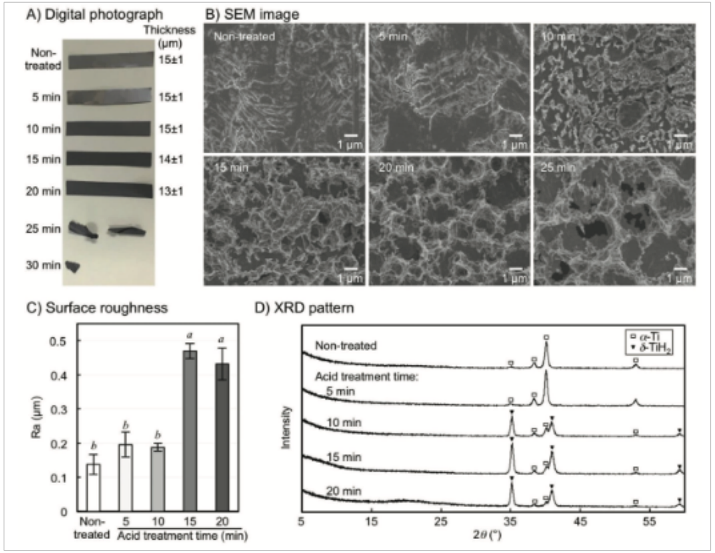
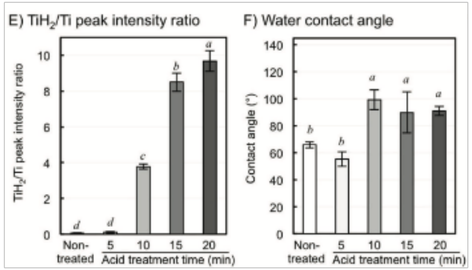
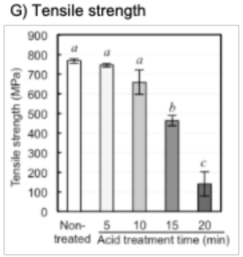
Supplementary information II: The influence of acid treatment time [*Adv. Mater. Interfaces* **7** (2020) 1902089; *J. Mater. Chem. B* **9** (2021) 8348]

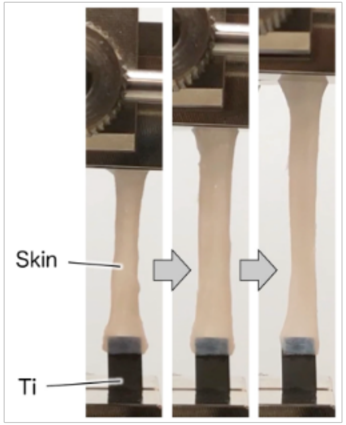
Influences of acid treatment time

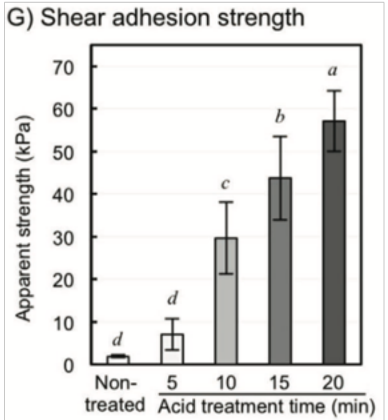




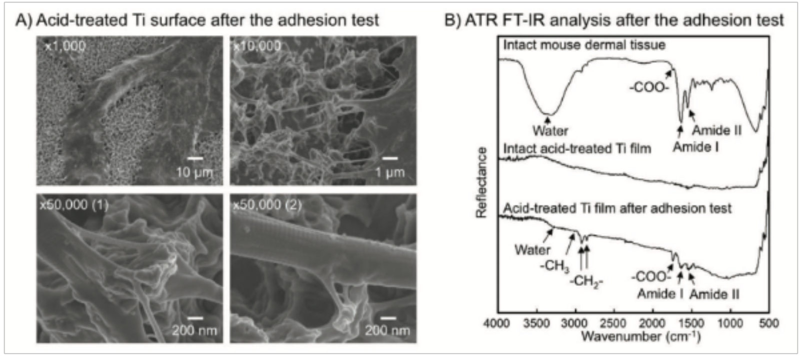


Immediate soft-tissue adhesion





The increased acid treatment time led to an increase in the soft-tissue adhesion strength of titanium films; Whereas the mechanical strength of the film decreased significantly after 20 min treatment. Therefore, the acid treatment time in this study was set to 15 min.



The protein adsorption on hydrophobic surfaces is much larger in adsorbed amount and faster in adsorption rate than that on hydrophilic surfaces [*J Am Chem Soc* **120** (1988) 3464]. One of the adhesion mechanisms of the acid-treated titanium would be hydrophobic interaction, judging from the increased water contact angle and hydrophobic components remained on the acid-treated titanium after the shear adhesion tests with mouse dermal tissues.

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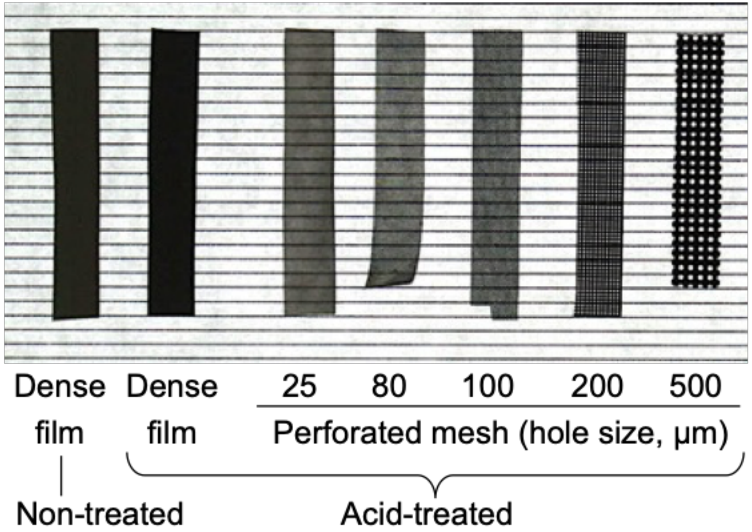
Supplementary information III: Digital photographs and SEM images of titanium meshes

Digital photographs



SEM images