Electrochemical property and corrosion behavior of multi-directionally forged titanium in fluoride solution

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Multi-directional forging (MDFing) can improve the various properties of metals and alloys due to the evolution of an ultrafine-grained structure. In the present study, electrochemical properties and corrosion behaviors in a fluoride solution of MDFed pure titanium (MDF-Ti) were evaluated by comparing with conventional coarse-grained pure titanium (Ti). The E_open value of MDF-Ti was significantly higher than that of Ti. However, similar potentiodynamic polarization profiles were obtained for Ti and MDF-Ti. Immersion in NaF solution caused no severe corrosion to Ti or MDF-Ti. However, immersion in acidulate phosphate fluoride solution (APF) revealed that MDF-Ti had better corrosion resistance than Ti at shorter time immersion periods and was more susceptible to corrosion for longer immersion. Significantly less release of titanium was observed for MDF-Ti in shorter immersion periods in APF. In conclusion, MDF-Ti showed similar electrochemical behaviors to Ti and less susceptible to corrosion in shorter time APF immersion.

Keywords: Multi-directional forging, Ultrafine grain, Titanium implant, Corrosion, Fluoride

INTRODUCTION

Commercially pure titanium (Ti) and Ti alloys have been commonly used as orthopedic or dental implants due to their tight bonding property to bone, known as osseointegration11. Ti alloys such as Ti-6Al-4V or Ti-6Al-7Nb have mechanical properties superior to those of Ti. However, it is claimed that released heavy metal ions bring risks of biological problems. For example, vanadium is cytotoxic and is known as a carcinogenic substance39. Aluminum is reported to be associated with the induction of neurotoxicity and neurodegenerative diseases, such as Alzheimer’s disease3). Thus, new titanium alloys such as Ti-Nb-Ta-Zr, Ti-Nb-Sn, or Ti-Mn without vanadium and aluminum have been developed4-7).

Another problem for Ti alloys is differences in the elastic modulus with bone. The elastic modulus of cortical bone was reported to be approximately 10–30 GPa, and that of Ti alloys such as Ti-6Al-4V was approximately 110 GPa4). These differences in elastic modulus can cause the uneven transmission of applied stress at the interface between bone and implant materials, which is called stress shielding; this uneven loading sometimes results in the loosening and/or fracture of titanium implants8,9). Sumitomo et al. investigated the healing of experimental fractures made in rabbit tibiae by bone plates with different elastic moduli and confirmed that elastic moduli of the bone plate will naturally influence the bone tissue reaction10.

On the contrary, decreasing the grain size can induce strengthening of the metallic material without the addition of any alloying elements, which is known as the Hall-Petch relation11-13). There are several methods for decreasing grain size by severe plastic deformation, such as accumulative roll bonding14), high pressure torsion15), equal channel angular pressing (ECAP)16), and multi-directional forging (MDF)17-19). Particularly, MDF is a useful method for preparing large samples, and there is little limitation of the shape, too. A schematic illustration for the MDF method is shown in Fig. 1. Forging strain was repeatedly applied while changing the forging axis as illustrated. Miura et al. applied the MDF method to Ti or magnesium alloys and reported their ultrafine-grained structures and notably high tensile strengths18,19). Transmission electron microscope observation revealed ultrafine-grained structure of MDFed pure titanium (MDF-Ti)19). For example, average grain size and the ultimate tensile strength of MDF-Ti grade 2 were finer than 100 nm and more than 1 GPa. The average grain size of conventional Ti was approximately 30 µm. Hoshi et al. reported that MDF-Ti showed higher tensile strength and Vickers hardness and a lower elastic modulus as compared to conventional pure Ti20). The elastic modulus of MDF-Ti was approximately 50 GPa. Lower elastic modulus was an attractive property of MDF-Ti as a dental implant material. Suzuki et al. investigated the bone response of MDF-Ti by animal experiments and reported that MDF-Ti showed bone response similar to that of Ti after implantation into the cortical bone of rabbits21). Arai et

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al. also reported that the promotion of osteoblast-like cell proliferation on MDF-Ti was more significant than that on conventional Ti by sulfuric acid treatment\(^{22}\). Ti has superior corrosion resistance due to the passive film formation in the body fluid environment. However, various studies have reported that the corrosion resistance of Ti or Ti alloys decreased with the treatment of a fluoride solution\(^{23-26}\). Corrosion behaviors are influenced by the concentration of fluoride, pH, etc. A decrease of pH caused the corrosion resistance of Ti\(^{27-29}\). MDF-Ti has an ultrafine-grained structure with a significantly high-volume fraction of grain boundaries. It is well known that corrosion takes place preferentially at some specific grain boundaries and, therefore, the change in the corrosion properties of Ti strongly depended on microstructure\(^{30}\). Hence, it is presumed that the corrosion resistance of MDF-Ti will differ from that of Ti. However, there are few reports regarding the behaviors of ultrafine-grained Ti prepared by severe plastic deformation after fluoride treatment. It is very important to investigate the influence of fluoride treatment on MDF-Ti for future dental clinical application.

In the present study, we first electrochemically examined the properties of MDF-Ti and then observed the changes of surface morphologies of MDF-Ti after immersion in two types of fluoride solution with different pH by comparing it with Ti.

**MATERIALS AND METHODS**

**Titanium substrate**

An MDF-Ti disk (φ: 15 mm; thickness: 1.0 mm; JIS 2 type; 99.9% mass; Kawamoto Heavy Industries, Hyogo, Japan)\(^{18,19}\) was compared to a commercially available pure Ti disk (φ: 15 mm; thickness: 1.0 mm; JIS 2 type; 99.9% mass; Furuuchi Chemical, Tokyo, Japan). MDF-Ti possesses an ultrafine-grained structure with high dislocation density, whereas the latter is coarse grained and with much lower dislocation density. Both were polished with #800 and #1200 waterproof paper and ultrasonically cleaned in distilled water, ethanol, and distilled water for 15 min. After cleaning, they were stored in a desiccator for one day.

**Electrochemical measurement**

Electrochemical measurements were performed in accordance with the procedures reported by Takemoto et al.\(^{31,32}\). The apparatus for electrochemical measurement consisted of a potentiostat/galvanostat (Model 263A, EG&G, Princeton Applied Research, USA), a saturated calomel electrode (SCE) as a reference electrode, a platinum plate as a counter electrode, and a sample holder (the exposed area of the specimen was 1.0 cm\(^2\) as a working electrode. A Ti or MDF-Ti disk was mounted on a sample holder. A volume of 500 mL of saline solution (0.9 mass% NaCl) was deaerated with pure nitrogen gas for 30 min before measurement. The open circuit potential (E\(_{\text{open}}\)) was measured after the specimen was immersed in the saline solution for 30 min. The potential dynamic polarization behavior of the specimen was recorded within a scanning range of −1.2 to +2.5 V (vs. SCE) as a scanning rate of 0.33 mV/s. Each measurement was maintained at 37°C. Four specimens were tested for each condition.

**Immersion in fluoride solution**

The fluoride solution consisted of 2 mass% NaF solution (pH=7.3) and Fluor N solution (Acidulate phosphate fluoride solution (APF), 9,000 ppm, pH=5.3, Bee Brand Medico Dental, Osaka, Japan). Fluor N solution is commonly used as tooth application products for carious prevention.

The Ti or MDF-Ti disk was immersed in 5 mL of each solution at 37°C. For NaF solution, Ti or MDF-Ti disk was immersed at 1, 3, and 7 days. On the contrary, Ti or MDF-Ti disk was immersed at 1, 3, and 6 h, and 1, 3, and 7 days in APF solution. After the immersions in each solution, the disks were rinsed with double-distilled water, and each specimen was dried in a desiccator. The morphology changes of Ti and MDF-Ti in NaF and APF at 1, 3 and 6 h immersion. The surface appearance of each disk before and after immersion in fluoride solution was observed by scanning electron microscopy (SEM; S4000, Hitachi High-Technologies, Tokyo, Japan) at an accelerating voltage of 5 kV after ion coating with gold.

The surface roughness of Ti and MDF-Ti after immersion in NaF or APF before and after immersion in the fluoride solution for 3 days was measured using a shape analyzer laser microscope (VK-X250, KEYENCE, Osaka, Japan). Images were acquired in three-dimensional ranges of decreasing sizes of 10×10 µm\(^2\). Two surface parameters, the three-dimensional arithmetic mean height (Sa), and the developed interfacial area ratio (surface deployment area rate; Sdr) were obtained.

**Titanium ion measurements in APF**

Released concentrations of titanium from Ti and MDF-Ti...
disk in APF solution were measured with an inductively coupled plasma emission plasma spectrometer (ICP, Vista-MPX, SII, Chiba, Japan)\(^3\). Ti and MDF-Ti disk was polished and cleaned as mentioned above, and were immersed in 10 mL of APF at 37°C. After 1, 3 and 6 h immersion, released concentrations of titanium ion were determined.

**Statistical analysis**
The results of the electrochemical measurements, surface roughness and released concentrations of titanium ion between Ti and MDF-Ti were evaluated by an unpaired \( t \)-test. Data for surface roughness, \( S_a \), and \( S_d \) of each material before and after immersion in fluoride solution and released concentrations of titanium ion at 1, 3 and 6 h were analyzed using a one-way analysis of variance and a post-hoc Tukey’s test for multiple comparisons among means. Statistical analyses were conducted with OriginPro 9.0 J (OriginLab, Northampton, MA, USA). \( p \) Values of less than 0.05 were considered significant, and data were expressed as the mean±standard deviation (SD).

**RESULTS**
The potentiodynamic polarization profiles of Ti and MDF-Ti are shown in Fig. 2. Both Ti and MDF-Ti showed similar profiles. Table 1 lists the values of \( E_{\text{open}} \) and the \( I_{0.5} \) obtained from the potentiodynamic polarization curves. The \( E_{\text{open}} \) value of MDF-Ti was significantly higher than that of Ti \(( p<0.05)\).

SEM pictures of the surfaces of Ti and MDF-Ti before and after immersion in fluoride solution are shown in Figs. 3–9. Before immersion, roughened surface by polishing was similarly observed on both Ti and MDF-Ti surfaces (Fig. 3). After immersion in NaF solution, the surfaces of Ti and MDF-Ti looked similar, and no distinct corrosion was observed during 7 days of immersion (Figs. 4, 5). Polishing scratches were still identified on both Ti and MDF-Ti surfaces even after immersion for 7 days (arrows in Figs. 4, 5).

On the contrary, APF immersion produced roughened surface of Ti and MDF-Ti by corrosion. Comparing the morphology changes of Ti and MDF-Ti among 1, 3, and 6 h immersion (Figs. 6, 7), Ti showed more roughened surface than MDF-Ti. Polished scratches were identified on MDF-Ti more clear than on Ti (arrows in Fig. 7). Only after 1 day immersion, more severely roughened surfaces of Ti and MDF-Ti were recognized (Figs. 8, 9). More uniform and progressed corrosion, developing complicated three-dimensional pitting structures, was observed on the MDF-Ti surface compared with Ti surface. This is reverse to the above-mentioned result. An ultrafine but three-dimensionally roughened structure was revealed by magnified observations of the macroscopically roughened structure.

|           | \( E_{\text{open}} \) (V) | \( I_{0.5} \) (µA/cm\(^2\)) |
|-----------|----------------------------|--------------------------|
| Ti        | \(-0.34 (0.02)^{a}\)       | 3.45 (0.57)^{a}\)         |
| MDF-Ti    | \(-0.29 (0.02)^{b}\)       | 3.34 (0.66)^{b}\)         |

\( ^{a,b} \): SD
Different small letters indicate a significant difference between Ti and MDF-Ti \(( p<0.05)\).
on the immersed MDF-Ti. Accumulated corrosion products were detected on the Ti surface, but not on the MDF-Ti surface. The above observations clearly indicate corrosion behaviors of MDF-Ti in NaF and APF solutions that are completely different from those of conventional Ti.

Figure 10 shows the titanium ion concentration released from Ti and MDF-Ti after the immersion in APF solution at 1, 3 and 6 h. Ti showed significantly higher titanium concentration than MDF-Ti (p<0.05). During 1
to 6 h immersion, there were no significant differences in titanium concentration for Ti and MDF-Ti ($p>0.05$).

Tables 2 and 3 show the surface roughness measurements. Sa and Sdr values significantly increased after immersion in APF for both Ti and MDF-Ti ($p<0.05$).

NaF immersion caused no significant increase in Sa and Sdr values ($p>0.05$). Comparing Ti and MDF-Ti, MDF-Ti showed Sa and Sdr values significantly greater than those of Ti ($p<0.05$) after immersion in APF. In the case of NaF immersion, there were no significant differences...
in Sa and Sdr values between Ti and MDF-Ti ($p>0.05$).

**DISCUSSION**

In the present study, we electrochemically examined the properties of MDF-Ti and observed the changes of surface morphologies of MDF-Ti after immersion in two types of fluoride solution with different pH by comparing it with Ti.

First, the electrochemical properties of Ti and MDF-
Ti were evaluated. The significantly higher $E_{\text{open}}$ value of MDF-Ti suggested a lower ionization tendency and more stable passive film of MDF-Ti. However, similar potentiodynamic polarization profiles were obtained for Ti and MDF-Ti. It is presumed that there were no distinct differences in the electrochemical properties of Ti and MDF-Ti. In the present study, electrochemical measurements were performed in a saline solution. Electrochemical properties in fluoride solution should be further investigated.

Corrosion by two types of fluoride solution of Ti and MDF-Ti was tested. One solution was a neutral NaF solution and the other an acidic fluoride solution, APF. NaF immersion caused no severe corrosion to either Ti or MDF-Ti. APF immersion is supposed to cause more severe corrosion on Ti and MDF-Ti. Thus, we performed corrosion experiments at shorter immersion periods (1, 3, and 6 h) for Ti and MDF-Ti, in addition to longer immersion periods (1, 3, and 7 days). As supposed, APF caused more severe corrosion to both Ti and MDF-Ti than NaF, which concurs with the findings of previous reports. Ide et al. suggested that the natural electron potential of Ti was decreased by the acidification of the NaF solution. They also insisted that the results of polarization resistance were similar to those of the natural electrode potential and that the decrease in pH decreased the polarization resistance, which readily caused the corrosion reaction with immersion in fluoride solution.

However, the results of shorter immersion periods were opposite to the results of longer immersion periods. Less corrosion of MDF-Ti was recognized for shorter immersion periods, and greater corrosion of MDF-Ti was observed for longer immersion periods. Measurements of titanium ion in APF also supported these results. Significantly less titanium concentration was observed for MDF-Ti in shorter immersion periods in APF. It revealed that MDF-Ti has a better corrosion resistance for early stage of APF immersion. The reason is not still clear, but it is speculated that the difference of passive oxide layer will influence the corrosion resistance. Ultrafine-grained structure of MDF-Ti may be active towards oxidation. Thus, more condensed and thicker passive oxide layer will be produced for MDF-Ti compared with Ti. As a results, MDF-Ti showed better corrosion resistance
Table 2  Arithmetical mean height (Sa) of Ti and MDF-Ti after immersion in NaF or APF (10×10 µm²)

|        | 0 days      | 3 days in NaF | 3 days in APF |
|--------|-------------|---------------|---------------|
| Ti     | 0.23 (0.06)a,A | 0.25 (0.04)b,B | 0.61 (0.09)b,D |
| MDF-Ti | 0.21 (0.05)b,A | 0.21 (0.04)c,C | 0.88 (0.20)d,D |

(     ): SD
Different letters indicate a significant difference (p<0.05).
Small letters indicate a difference between before and after immersion in fluoride solution at 3 days with the same material. Large letters indicate a difference between Ti and MDF-Ti at 0 days and after 3 days of immersion in NaF and APF, respectively.

Table 3  Developed interfacial area ratio (Sdr, %) of Ti and MDF-Ti after immersion in NaF or APF (10×10 µm²)

|        | 0 days      | 3 days in NaF | 3 days in APF |
|--------|-------------|---------------|---------------|
| Ti     | 30.31 (7.93)a,A | 30.79 (3.54)b,B | 178.73 (52.22)b,D |
| MDF-Ti | 27.99 (5.74)c,A | 27.35 (5.82)c,C | 675.40 (126.66)d,D |

(     ): SD
Different letters indicate a significant difference (p<0.05).
Small letters indicate a difference between before and after immersion in fluoride solution after 3 days with the same material. Large letters indicate a difference between Ti and MDF-Ti at 0 days and after 3 days of immersion in NaF and APF, respectively.

in APF at the early stage of the immersion. But when passive oxide film is destroyed, corrosion progresses along ultrafine crystal grain boundaries for MDF-Ti. As a result, MDF-Ti will be more susceptible to corrosion by acidic fluoride solution for longer immersion periods more than 1 day. The detailed analysis for passive oxide layer of MDF-Ti should be further investigated.

Takemoto et al. reported the formation of titanium-fluoride compounds on the Ti surface32), but present study showed there no corrosion products on MDF-Ti surface after APF immersion. The reason not still clear. But it is presumed that ultrafine-grained structure and uniform multi-directional processing influenced the corrosion mechanism of MDF-Ti including the hydrogen adsorption. More detailed analysis should be needed.

However, in the oral environment, a Ti prosthesis is covered with proteins such as albumin. Some reported that the presence of albumin suppressed the corrosion of titanium28,31-35). It is postulated that albumin adsorption on Ti prevented the attack of fluoride or that the buffering effect of the albumin increased the pH surrounding the Ti materials. Moreover, the time of exposure of Ti prostheses to fluoride solution may be only a few minutes in oral conditions. Uchiyama et al. alternately immersed Ti in fluoride solution and in artificial saliva solution and found no significant differences in color and in surface morphologies of Ti before and after immersion36). In the present study, MDF-Ti showed better corrosion resistance during 6 h immersion. We can conclude that corrosion of MDF-Ti towards acidic fluoride solution will not cause severe damages in clinical conditions. Evaluation of corrosion resistance of MDF-Ti in a condition that simulates the intraoral environment should be needed.

Another point of view of uniform and ultrafine roughened structures of MDF-Ti by fluoride corrosion suggests that acid or alkali treatment will produce similar structures on the surface of MDF-Ti. Arai et al. reported that sulfuric acid treatment of MDF-Ti produced much finer and equiaxed pitting features as compared to those of Ti, and fractal pitting structures regularly and uniformly developed on the surface of MDF-Ti22). Macro and micro roughened structures of MDF-Ti will be expected to exhibit better biocompatibility, for example new bone formation or bone growth. The influence of acid or alkali treatment of MDF-Ti on bony tissue will be further investigated for developing new types of dental implants.

In conclusion, MDF-Ti's electrochemical behaviors are similar to those of Ti, and it is more susceptible to corrosion by acidic fluoride solution. Fluoride corrosion produced uniform and ultrafine roughened pitting structures of MDF-Ti. The pitting structures appeared to be three-dimensionally complicated.

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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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