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Frictional Coefficients of the Passive Titanium Surfaces Evaluated with *In-situ* and *Ex-situ* Nano-scratching Tests

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Abstract

In-situ (kept at 5 V or 0 V in solution) and *ex-situ* (in air after anodic oxidation) nano-scratching tests by using the Berkovich pyramidal diamond indenter were performed to evaluate the friction coefficient of the polycrystalline titanium surface anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution. The friction coefficients of the titanium surfaces obtained with *in-situ* nano-scratching were significantly larger than those obtained with *ex-situ* nano-scratching. Moreover, the *in-situ* friction coefficient of the titanium surface kept at 5 V (RHE) was larger than that of the titanium surface kept at 0 V (RHE). Based on the large difference in AFM images of the scratched area after *in-situ* and *ex-situ* nano-scratching and on the stick-slip like a phenomenon observed only during *in-situ* nano-scratching, it has been proposed that a series of mechano-electrochemical reaction such as the film rupture, anodic dissolution from the rupture sites and the repassivation, takes place at the moving front of the indenter tip during *in-situ* nano-scratching, and the promotion of the repassivation gives the high impedance against the movement of the indenter tip. The large friction coefficient obtained with *in-situ* nano-scratching was explained in terms of the promotion of the repassivation by the large potential difference between the titanium substrate and solution.

Keywords: Nano-scratching, Friction coefficient, Mechano-electrochemistry,

Titanium, Passive film,

Introduction

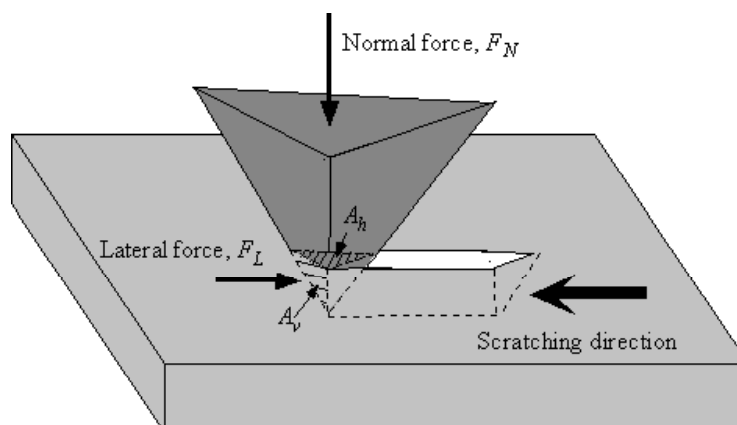
Titanium has the high corrosion resistance in oxidative environment, which is mainly brought by the stable surface oxide film, i.e., passive film, and is used in the severe corrosion environment. Moreover, titanium has the excellent conformity to a living body and is used in a living body as artificial bones or joints. The physico-chemical and mechanical properties of the passive titanium surface are important for the practical uses of titanium. There have been many studies on the physico-chemical properties of the passive titanium. In contrast, there have been few studies on the mechanical properties.

Nano-indentation and nano-scratching techniques have been recently developed to evaluate the mechanical properties (hardness, elastic modulus and friction coefficient) of surface thin films. Most of nano-indentation and nano-scratching tests were performed in air. The mechanical properties of the passive titanium surface kept in solution may be different from those measured in air after removal from the solution. When titanium is used in solution, it is essentially necessary to evaluate the mechanical properties of the titanium surface kept in solution. In our previous studies [1–3], nano-indentation and nano-scratching tests in solution as well as in air were performed on the passive iron and titanium surfaces kept in solution to evaluate the hardness and friction coefficient in solution and in air.

In the present study, nano-scratching tests in solution (*in-situ*) as well as in air (*ex-situ*) were performed on the passive titanium surface kept at a constant potential in pH 8.4 borate solution to investigate more in detail the difference between the friction coefficients in solution and in air.

Experimental

Polycrystalline titanium disk-plate with a diameter of 10 mm and a thickness of 2 mm was used for experiments. The titanium specimen was mechanically polished with alumina abrasives and then finally electropolished with a constant cell voltage of 70 V in a mixture of methanol, 2-methoxyethanol, 2-ethoxyethanol and perchloric acid at - 75°C to remove the worked layer (Beilby layer) existing on the mechanically polished surface. The electrolyte solution employed was pH 8.4 borate solution. A small electrochemical cell made from Diflon was specially designed for nano-scratching in solution (*in-situ*). A platinum ring and wire were used as counter and reference electrodes, respectively. The potential of the platinum wire was always measured with an Ag/ AgCl reference electrode for calibration before and after every experiment. The electrode potential of the specimen was converted to a reversible hydrogen electrode (RHE).



The transducer for nano-scratching (Hysitron Inc.) was attached to the AFM (Digital Instruments, Nanoscope IIIa) in which the electrochemical cell was set. A Berkovich pyramidal diamond tip was employed for nano-scratching and attached to a tungsten rod for use in liquid. The titanium specimen was anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution at 25 °C to form the anodic oxide film on it. It is known that the thickness of anodic oxide film formed on titanium at 5 V (RHE) for 1 h in pH 8.4 borate solution is about 15 nm [4]. The *in-situ* nano-scratching was performed on

Fig. 1 Schematic illustration of nano-scratching was performed on the specimen surface kept at 5 V (RHE) in pH 8.4 borate solution after anodic oxidation. The *ex-situ* nano-scratching was also performed on the specimen taken out from the solution into air after anodic

oxidation, washed with milli-Q filtered water and dried with a jet of nitrogen gas.

As shown schematically in Fig. 1, the one triangle plane without ridge of the Berkovich diamond tip was moved to the lateral direction at a scratching rate of $1 \mu\text{m s}^{-1}$ between a distance of $2 \mu\text{m}$ and the lateral force, F_L , was measured as a function of scratching distance under a constant normal force, F_N . The friction coefficient, μ' , is defined with dividing F_L by F_N .

$$\mu' = F_L / F_N \quad (1)$$

Results and Discussion

Figures 2 and 3 show the AFM images and height-profiles of the scratched area after *in-situ* and *ex-situ* nano-scratching at a constant normal force of $F_N = 300 \mu\text{N}$, respectively for the titanium surfaces anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution. The grooves produced by the scratching and the resultant protrusions can be observed from these figures. It should be noted that the shapes of the grooves and protrusions are quite different between *in-situ* and *ex-situ* nano-scratching in spite of the same scratching conditions. In Figs. 4 and 5, the displacement in normal direction, D_N , and the lateral force, F_L , are plotted as a function of displacement in lateral direction, D_L , during *in-situ* and *ex-situ* nano-scratching at a constant normal force of $F_N = 300 \mu\text{N}$, respectively, for the titanium surfaces anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution. The normal

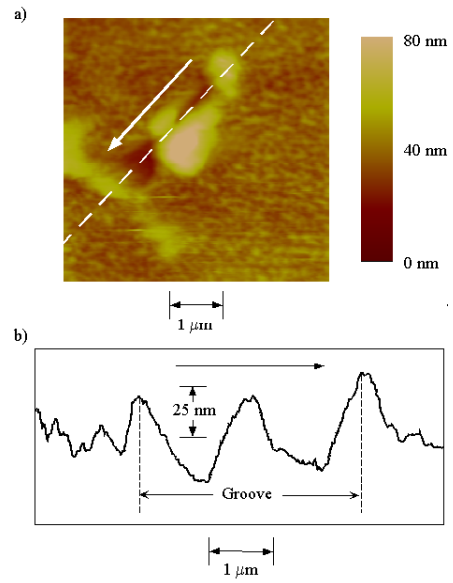
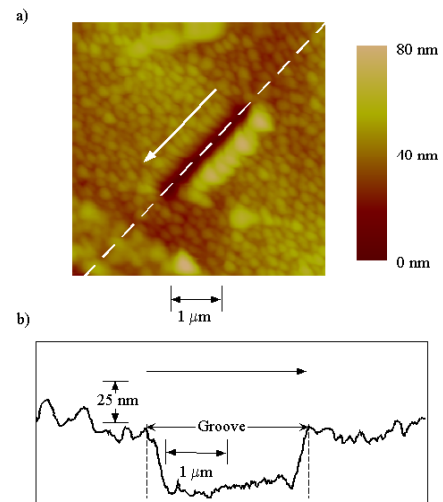


Fig. 2 a) AFM image of the scratched area after *in-situ* nano-scratching for the titanium surface anodically oxidized at 5 V (RHE) for 1 h



displacement, D_N , before *in-situ* nano-scratching is less by about 50% than that before *ex-situ* nano-scratching, reflecting the difference between hardness obtained with *in-situ* and *ex-situ* nano-indentation [3].

In case of *ex-situ* nano-scratching, both D_N and F_L increase within a short lateral displacement, $D_L = 0.2 \mu\text{m}$ and attain a steady state with a small fluctuation. In contrast, in case of *in-situ* nano-scratching, D_N decreases with lateral displacement, D_L , while F_L increases and attains a steady state accompanying a large periodic fluctuation. This *in-situ* nano-scratching behaviour is similar to a stick-slip phenomenon often observed in the system with large difference between static and dynamic friction coefficients [5]. The large periodic fluctuation in F_L may not be related to the grain boundary of the polycrystalline titanium surface, because the average grain size (several μm) obtained with SEM observation of the titanium surface was larger than the periodic distance of about $0.5 \mu\text{m}$. The normal displacement, i.e., scratch depth changes from 22 nm to 10 nm during *in-situ* nano-scratching, while it changes from 40 nm to 43 nm during *ex-situ* nano-scratching. As seen from Figs. 4 and 5, the averaged normal displacement, D_N , i.e., scratch depth during *in-situ* nano-scratching is almost the same as the film thickness (15 nm). On the other hand, the averaged scratch depth during *ex-situ* nano-scratching is 2.8 times as much as the film thickness. It is drawn from the above comparison that during *in-situ* nano-scratch but also the substrate titanium scratching.

Figure 6 shows the friction coefficient μ' for *in-situ* and *ex-situ* nano-scratching. The *in-situ* value of μ' was determined from the slope of the F_L vs. D_L curve. The *ex-situ* value of μ' was determined from the slope of the F_L vs. D_L curve.

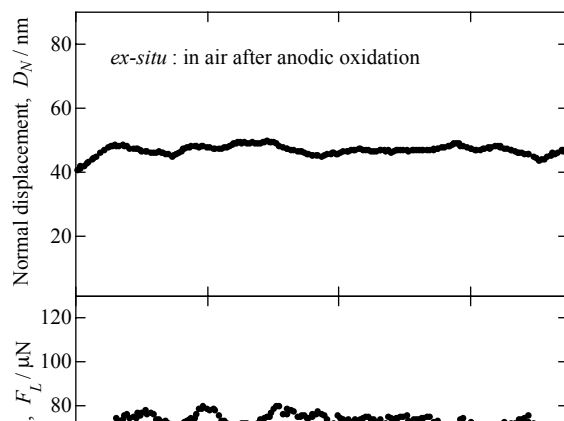


Fig. 5 D_N and F_L as a function of D_L during *ex-situ* nano-scratching with a rate of $1 \mu\text{m s}^{-1}$ at $F_N = 300 \mu\text{N}$ for the titanium surface anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution.

situ value of μ' for the titanium surface kept at 0 V (RHE) after anodic oxidation at 5 V (RHE) for 1 h in pH 8.4 borate solution was also plotted versus normal force, F_N . The *in-situ* values of μ' have large fluctuation because of the stick-slip like phenomenon observed during *in-situ* nano-scratching. Therefore, it is difficult to find the normal force dependence of the *in-situ* values because of the large fluctuation. Nevertheless, it should be remarked that the averaged *in-situ* values of μ' for the titanium surfaces kept at 5 V (RHE) in pH 8.4 borate solution exceed unity. Moreover, the averaged *in-situ* values of μ' for the titanium surface kept at 0 V (RHE) after anodic oxidation at 5 V (RHE) in pH 8.4 borate solution are less than those for the titanium surfaces kept at 5 V (RHE) in pH 8.4 borate solution. In contrast, the *ex-situ* values of μ' have a small fluctuation and their averaged values increase from 0.19 to 0.28 with increasing normal force in the range of $F_N = 100\text{--}800\text{ }\mu\text{N}$.

It is generally accepted that the lateral force, F_L , consists of adhesion term, F_a and ploughing term, F_p , [6,7].

$$F_L = F_a + F_p \quad (2)$$

The adhesion term, F_a , is given by

$$F_a = s A_h \quad (3),$$

where s is the shear strength at the scratched interface of materials and A_h is the horizontal cross sectional area of the indenter tip in contact with the materials surface. The hardness,

H , of materials is defined with dividing F_N by A_h . F_a is thus given by

$$F_a = s (F_N / H) \quad (4).$$

On the other hand, the ploughing term, F_p , is represented by

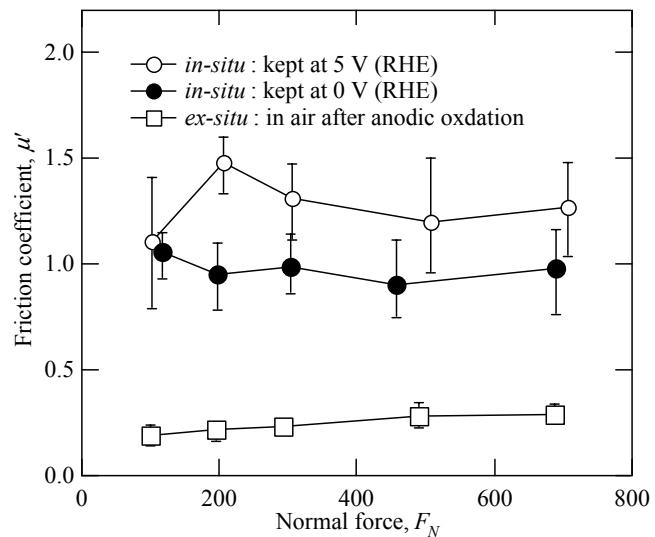


Fig. 6 μ' obtained with *in-situ* (kept at 5 V or 0 V in solution) and *ex-situ* (in air after anodic oxidation) as a function of F_N for the

$$F_p = p_f A_v \quad (5),$$

where p_f is the plastic flow pressure of materials against nano-scratching to the lateral direction and A_v is the vertical cross sectional area of the indenter tip in contact with the materials surface. The ratio of A_v to A_h is constant and determined by the geometry of Berkovich diamond indenter [7]. By taking into account the constant ratio, $k = A_v / A_h$, F_p is eventually given by

$$F_p = k p_f (F_N / H) \quad (6).$$

If substituting Eqs. (4) and (6) into Eq. (2), μ' can be represented by

$$\mu' = (s / H) + (k p_f / H) \quad (7).$$

The estimated shear strength, s , of polycrystalline titanium is in the range of 200–300 MPa. In our previous results of hardness measurement by nano-indentation, the *in-situ* value of H measured at a normal force of $F_N = 300 \mu\text{N}$ for the titanium surface kept at 5 V (RHE) in pH 8.4 borate solution was about 9 GPa, while the *ex-situ* value of H at the same normal force was 2 GPa [3]. If the above values of H are employed for calculation of the adhesion term, the contributions of the adhesion term to μ' are 0.02–0.03 and 0.1–0.15 for *in-situ* and *ex-situ* nano-scratching at a normal force of $F_N = 300 \mu\text{N}$, respectively.

It has been considered that the plastic flow pressure, p_f , is equivalent to the hardness, H , [7]. Assuming that the Berkovich pyramidal tip has an ideal geometry, $k = 0.27$, i.e., the contribution of ploughing term to μ' is 0.27, irrespective of *in-situ* and *ex-situ* nano-scratching. The net friction coefficients obtained from the above calculation, therefore, are 0.29–0.30 and 0.37–0.42 for *in-situ* and *ex-situ* nano-scratching, respectively. As seen from Fig. 6, the measured *in-situ* value of μ' at a normal force of $F_N = 300 \mu\text{N}$ is 1.3, which is 4.4 times as much as that calculated. In contrast, the measured *ex-situ* value of μ' at a normal force of $F_N = 300 \mu\text{N}$ is 0.24, which is less by 40 % than that calculated. According to the calculation, the contribution of adhesion term to the measured *in-situ* value of μ' should be negligibly small as compared with that of ploughing term.

The large deviation of the measured *in-situ* value of μ' from the calculated value and also from the measured *ex-situ* value may be associated with the ploughing term. Particularly, this large deviation may be explained in terms of the ploughing term only if the plastic flow pressure, p_f , is not equivalent to the hardness, H .

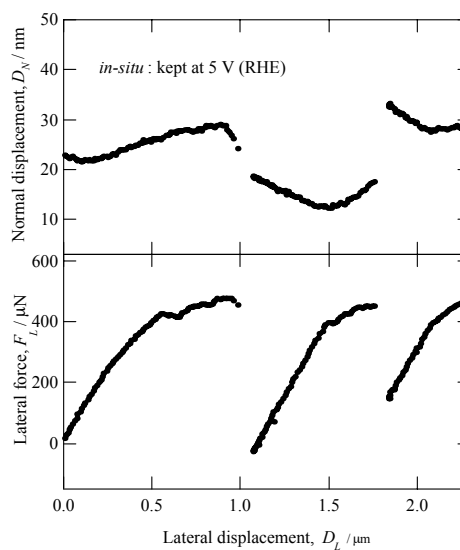
A series of mechano-electrochemical reaction on the titanium surface such as the film rupture, active dissolution of titanium from the substrate and the repassivation at the rupture sites would take place at the moving front of the indenter tip during *in-situ* nano-scratching. On the other hand, at the moving front of the indenter tip during *ex-situ* nano-scratching, the film rupture and oxidation, i.e., the repassivation only by air at the rupture sites would take place. Since in case of *in-situ* nano-scratching, the titanium surface is kept in the passive state at 5 V or 0 V (RHE), the anodic dissolution of titanium from the film rupture sites and followed by the repassivation at the rupture sites due to direct formation of anodic oxide or precipitation of hydrous oxide are promoted by a potential difference between the substrate titanium and the solution or a high electric field. In contrast, in case of *ex-situ* nano-scratching, no active dissolution occurs from the film rupture sites and the repassivation at the rupture sites is not promoted in the absence of high electric field and it is only brought by air-oxidation.

The movement of the indenter tip at the front of *in-situ* nano-scratching will be impeded by the rapid growth of anodic oxide or the instantaneous precipitation of hydrous oxide at the rupture sites, which increases apparently the plastic pressure, p_f , and leads to the large friction coefficient. Moreover, if newly produced anodic oxide or precipitated hydrous oxide at the rupture sites is strongly adhered to the moving front of the indenter tip, the indenter tip has to move accompanying the growing oxide or hydroxide, which increases not only the plastic flow pressure, p_f , but also the area ratio, k , and thus contributes to the increase in friction coefficient. The sticky adhesion of oxides to the indenter tip and the high impedance against its movement are plausible as seen from the AFM images in Figs. 2 and 3. The AFM images indicate that the edge of the groove produced by *in-situ* nano-scratching is not linear and the distribution and size of

protrusions are not uniform as compared with *ex-situ* nano-scratching. The stick-slip like a phenomenon observed during *in-situ* nano-scratching may result from the repeated adhesion and fall off of newly grown oxides as supported by the clear difference in AFM images between *in-situ* and *ex-situ* nano-scratching.

It is expected that the repeated adhesion and fall off of newly grown oxides becomes more significant in the lower scratching rate. Figure 7 shows the displacement in normal direction, D_N , and the lateral force, F_L , as a function of displacement in lateral direction, D_L , during *in-situ* nano-scratching at a rate of $0.17 \mu\text{m s}^{-1}$ at a constant normal force of $F_N = 300 \mu\text{N}$ for the titanium surfaces anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution. It is seen from Fig. 7 that the stick-slip like a phenomenon becomes more distinct, indicating the additional support of the repeated adhesion and fall off of newly grown oxides. The difference in measured *in-situ* values of μ' between the titanium surfaces kept at 5 V and 0 V (RHE) can be explained by a series of mechano-electrochemical reaction taking place at the moving front of the indenter. The anodic dissolution of titanium from the film rupture sites and followed by the repassivation at the rupture sites due to direct formation of anodic oxide or precipitation of hydrous oxide are more promoted at 5 V than at 0 V (RHE), because of the large potential difference or the high electric field and thus μ' for the titanium surface kept at 5 V (RHE) is larger than that for the titanium surface kept at 0 V (RHE).

It has been proposed from the above discussion that the friction coefficient is strongly influenced by a series of mechano-electrochemical reaction taking place at the moving front of the indenter tip during *in-situ* nano-scratching. Further experiments, however, are needed to elucidate the



validity of this new proposal.

Conclusions

In-situ (kept at 5 V or 0 V in solution) and *ex-situ* (in air after anodic oxidation) nano-scratching tests were performed on the polycrystalline titanium surfaces anodically oxidized at 5 V (RHE) for 1 h in pH 8.4 borate solution to evaluate the friction coefficient. The following conclusions were drawn for the friction coefficients of the passive titanium surfaces.

Fig. 7 D_N and F_L as a function of D_L during *in-situ* nano-scratching with a rate of $0.17 \mu\text{m s}^{-1}$ at $F_N = 300 \mu\text{N}$ for the

The friction coefficients of the passive titanium surfaces obtained with *in-situ* nano-scratching were significantly larger than those obtained with *ex-situ* nano-scratching. Moreover, the *in-situ* friction coefficient of the passive titanium surface kept at 5 V (RHE) was larger than that of the passive titanium surface kept at 0 V (RHE).

The AFM images of the scratched area after *in-situ* and *ex-situ* nano-scratching indicated that the edge of the groove produced by *in-situ* nano-scratching was not linear and the distribution and size of the protrusions were not uniform as compared with *ex-situ* nano-scratching. The stick-slip like a phenomenon was observed only during *in-situ* nano-scratching, which was reflected on the AFM images.

To explain the large friction coefficient obtained with *in-situ* nano-scratching as compared with *ex-situ* nano-scratching, it has been proposed that a series of mechano-electrochemical reaction such as the film rupture, active dissolution from the rupture sites and the repassivation takes place at the moving front of the indenter tip during *in-situ* nano-indentation, and the promotion of the repassivation by the large potential difference between the substrate titanium and solution gives the high impedance against the movement of the indenter tip to increase the friction coefficient.

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