In Situ Observation on Localized Corrosion Morphology of TiN Thin Film Coating by Electrochemical AFM

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ABSTRACT

Ceramic thin film was widely used due to its superior mechanical and chemical characteristics. However, defects and micro cracks were always existed from the initial stage. Depending on these various factors, localized corrosion was generated and developed into micro-cracks in some cases, when ceramics coating was applied in corrosive environment. Especially, correlation between corrosion morphology and the state of interface were important. However, these correlations were not evaluated in detail. Because of the better understanding of correlation between localized corrosion progress and defect morphology of thin film coating, in situ observation in aqueous solution together with electrochemical measurement was needed. Therefore, in situ observation of defect morphology and nm or μm orders localized corrosion generated in 3% NaCl aqueous solution was conducted by Electrochemical Atomic Force Microscopy (EAFM) newly established by present authors. To understand the correlation between ceramic film coating method and localized corrosion morphology, two different types of specimens, that is, specimens with and without effective previous treatment which have different interfacial strength. In case of TiN thin film coating with effective adhesive strength between substrate and coating, localized corrosion was not recognized into 3 % NaCl aqueous solution on pinhole defect. However, localized corrosion generated in dust entrained defect on same TiN thin film. On the other hand, In case of TiN film with incomplete adhesive strength, localized corrosion was recognized by EAFM. Therefore, to improve the corrosion resisting character of TiN thin film it is necessary to eliminate the entrained dust and to establish superior adhesion strength between TiN and substrate.

1. INTRODUCTION

Ceramic coating was widely used as thin coating technology due to superior corrosion resistance, wear resistance and high hardness [1, 2)]. However, various types of defect in nm or μm levels such as pinhole defect and crack were inevitably existed in thin film due to coating formation process. Depending on these various factors, localized corrosion was generated and even developed into micro-cracks in some cases, when ceramics coating was applied in corrosive environments [2, 3)].

On the other hand, to evaluate of corrosion resistance of ceramic thin film coating, the electrochemical potential seep methods were employed due to superior reproducibility and simply experimental procedure [2-4)]. However, under relatively severe experimental condition, corrosion pit was not necessarily formed depending on the difference of corrosion resistance, for example various types of defects. Because of the better understanding of correlation between localized corrosion progress and defect morphology of thin film coating, in situ observation in aqueous solution together with electrochemical measurement was needed.

In situ observation of defect morphology [5, 6] and nm or μm orders localized corrosion generated on various types of defects in 3% NaCl aqueous solution was conducted by Electrochemical Atomic Force Microscopy (EAFM) newly established by present authors. And also, difference in localized corrosion behavior in relation to kinds of defects, the previous treatment of interface between thin film coating and substrate and film thickness were evaluated.

2. EXPERIMENTAL PROCEDURES

2.1 Formation of TiN thin film coating

Specimen used in this study was 0.5 μm thick TiN thin film coated on AISI304 stainless steel by Dynamic Ion Mixing (DIM) method [7]. Because, DIM coated film was expected to have superior adhesive strength between substrate and coating. TiN thin film coatings were controlled by the rate of titanium and nitrogen deposition. Table 1 showed the chemical composition of AISI304 stainless steel substrate.

Previous treatment of N_2 ion bombardment was carried out for cleaning and for obtaining graded structure on substrate. For understanding the correlation between thin film formation method and localized corrosion morphology, two types of specimens with different previous treatments were used in this study. Specimen No. 17 has effective graded structure on substrate, on the other hand, specimen No. 18 has imperfect previous treatment. Table 2 showed various conditions of TiN coating by Dynamic Ion Mixing.

The structure of TiN ceramic coated layer was investigated by X-ray Diffraction. Also, depth profiles of chemical compositions on TiN coating were examined by X-ray Photoelectron Spectroscopy (XPS) . Figure 1 showed the results of X-ray Diffraction, and Figure 2 showed XPS depth profiles of TiN coating. The types of defects and the surface morphologies of TiN thin film coating were observed by optical microscope and FE-SEM.

Table 1 Chemical composition of AISI304 stainless steel.

Elements	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N
mass%	0.07	0.55	1.18	0.028	0.003	8.4	18.11	0.03	0.02	0.04

Table 2 Experimental condition of TiN thin film coating.

Condition of Previous treatment		Condition of TiN formation	
Target	AISI304	Base pressure	6×10^{-4} Pa
Base pressure	6×10^{-4} Pa	N_2 gas pressure	1×10^{-2} Pa
N_2 gas pressure	1×10^{-2} Pa	Ti evaporation rate	0.6 nm/s
N_2 ion beam current	100 $\mu A/cm^2$	N_2 ion beam current	42 $\mu A/cm^2$
N_2 ion beam energy	20 keV	N_2 ion beam energy	20 keV
N_2 irradiation time	500 sec	Coating time	766 sec
YEW current	22 mA	Substrate temperature	573 K
		Thickness	0.5 μm
		YEW current	11.8 mA

2.2 In situ observation of localized corrosion morphology by Electrochemical AFM

For examining the localized corrosion morphology of TiN thin film coating in aqueous solution together with controlling the electrochemical conditions, in situ observation system of Electrochemical Atomic Force Microscopy combined with environmental control cell was established. Figure 3 showed the schematic diagram of EAFM system. Specimen surface with test area of 0.25 cm^2 exposed to the 3% NaCl aqueous solution was covered by silicone.

Also, polarization curve were measured by electrochemical methods under coupling condition using three electrodes method composed of specimen (working electrode) and Pt (counter electrode and referential electrode). The sweep rate was selected 0.3 mV/sec, sweep potential range was selected from 0V to +2V. The in situ observation of localized corrosion morphology generated at thin film coating defect were observed by CCD and AFM.

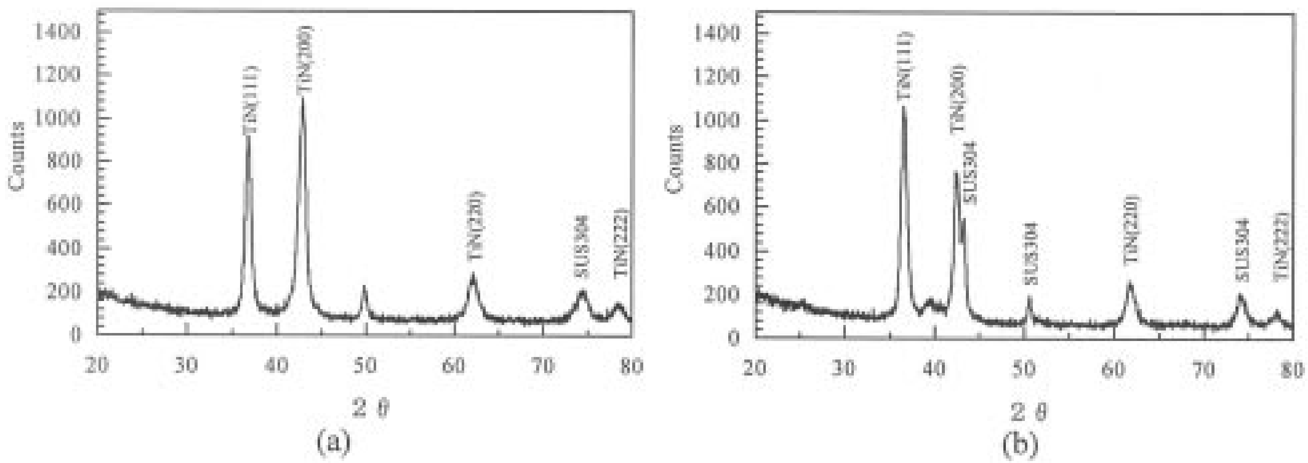


Figure 1 X-ray diffraction patterns of TiN thin film coating. (a) No. 17 (b) No. 18.

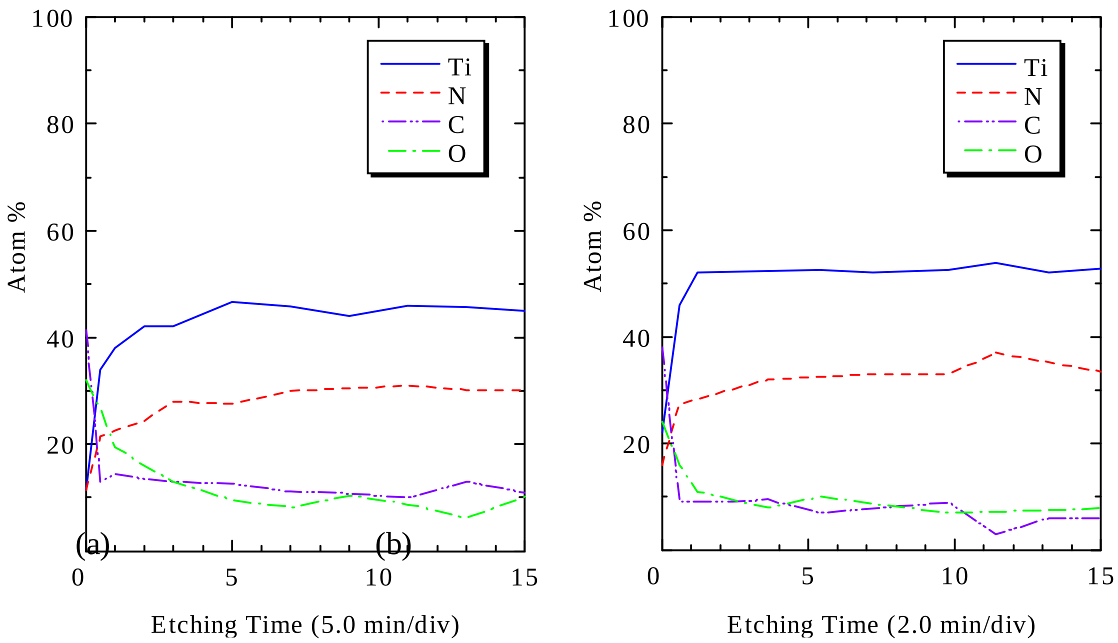


Figure 2 Depth profile of X-ray Photoelectron Spectroscopy investigation. (a) No. 17 (b) No. 18.

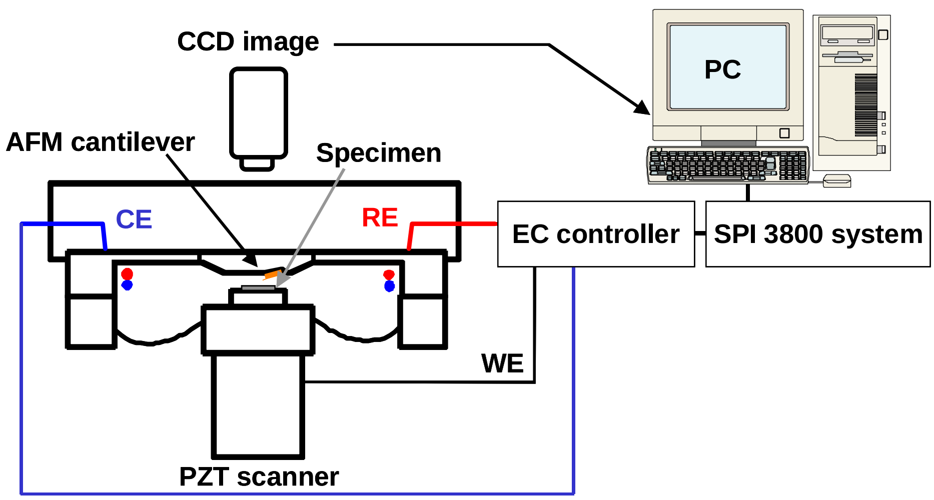


Figure 3 Schematic illustration of Electrical Chemical AFM system.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 In situ observation on localized corrosion morphology on coated TiN thin film by Electrochemical AFM

In this study, employing TiN thin film coating No.17 [7], two types of defects, this is, pinhole and entrainment impurity dust defects were observed by optical microscope and AFM. In case of TiN thin film coating with sufficient adhesive strength between substrate and coating, localized corrosion was not recognized on pinhole defect in coated TiN thin film during 200 hours immersions into 3 % NaCl aqueous solution. This pinhole defect was observed as relatively large size defect before the corrosion test. In contrast, pitting corrosion of substrate was generated on dust entrained defect in the same TiN thin film specimen.

Therefore, the correlation between localized corrosion behavior and the kinds of defects in film which existed from the initial stage was recognized in TiN thin film. In situ observation of localized corrosion morphology of TiN thin film coating was conducted by Electrochemical AFM. The polarization curve of No. 18 TiN thin film obtained by Electrochemical AFM was shown in Figure 4. Although the increase of current density was confirmed from the same figure, the current density (10μ A/cm^2) as pitting corrosion was not obtained. Therefore, this thin film coating showed superior corrosion resistance. However, observation of surface morphology in micro or nm order, localized corrosion morphology was confirmed on entrainment dust defects (Figure 5). At this time, localized corrosion morphology from pinhole defect in micro order was not observed.

As the same correlation between localized corrosion behavior and the kinds of defect on coated TiN thin film were observed in the long time immersions corrosion test results in 3% of NaCl aqueous solution, this experimental procedure were understood as effective method for examining the dependency of the kinds of thin film defects upon corrosion behavior. Therefore, by using Electrochemical AFM in situ observation, the localized corrosion process of TiN thin film in aqueous solution can be fully understood.

3.2 Effect of previous treatment upon localized corrosion morphology

To improve the adhesive state of interface between coated thin film and substrate previous treatment of N_2 ion irradiation was carried out. However, state of interface between thin film and substrate was changed depending upon the difference in the removed state of passive film on AISI304 stainless steel. Therefore, the passive film on substrate of No. 18 TiN thin film coating was incompletely removed, this specimen showed inferior corrosion resistance in polarization curve. And also, exfoliation of interface between coated thin film and substrate was recognized by observation of surface morphology after corrosion test.

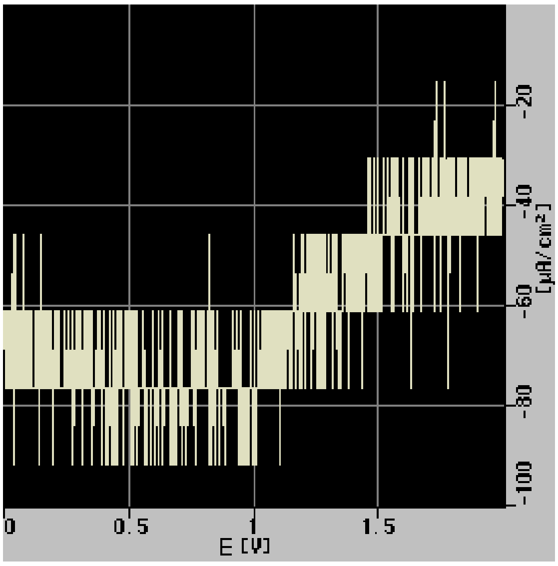
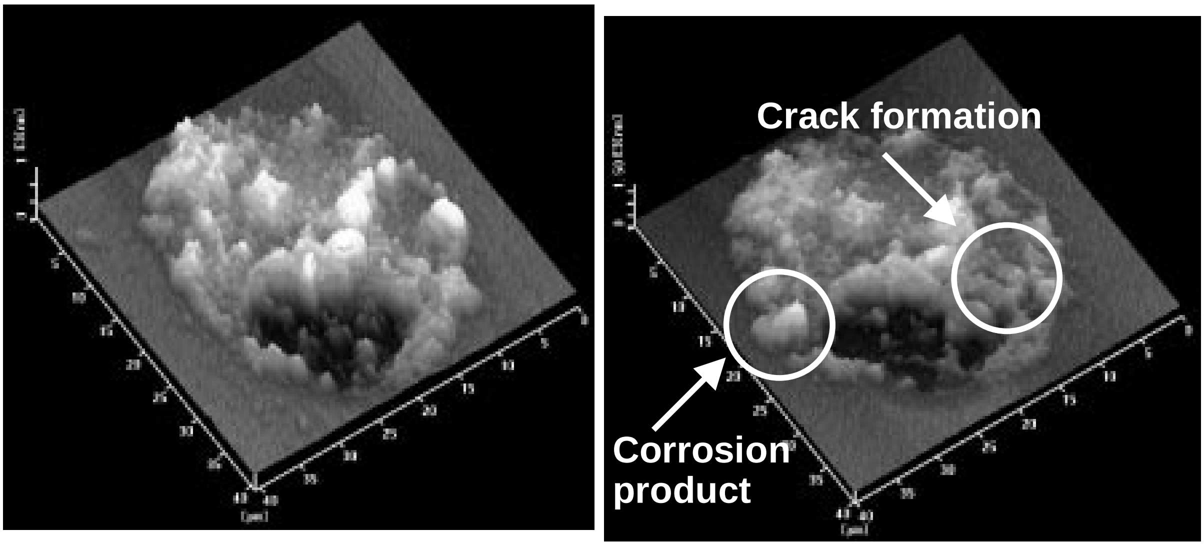


Figure 4 Polarization curve of TiN thin film coating (No.17) in 3% NaCl aqueous solution at 297K.



(a) (b)

Figure 5 Corrosion morphology of defect concerning contaminating dust on thin film.
(a) before corrosion test (b) after corrosion test

Therefore, the localized corrosion process of interface between TiN thin film and substrate was investigated by Electrochemical AFM under constantly increasing potentiostatic condition. The obtained result of polarization curve by Electrochemical AFM for coated TiN thin film No. 18 was shown in Figure 6. In the case of this specimen, different corrosion behavior was seen, i.e., the corrosion products were generated on pinhole defect after Electrochemical AFM measurement. However, the localized corrosion behavior of this specimen was governed by the generation of the pitting corrosion of substrate which caused the exfoliation of TiN thin film coating itself. This localized corrosion progressed along the grain boundary of substrate with the increased of the controlling potential.

From these results, it was understood that the location corrosion was generated at the entrainment dust defects in coated TiN thin film, when the suitable pretreatment was conducted. On the contrary, when the adhesive state between TiN film and substrate was not established, crevice corrosion and pitting corrosion at grain boundary of substrate were generated. Then, local exfoliation of TiN thin film was caused due to the acceleration of the localized corrosion. Therefore, to improve the corrosion resisting character of TiN thin film it is necessary to eliminate the entrained dust and to establish superior adhesion strength between TiN and substrate.

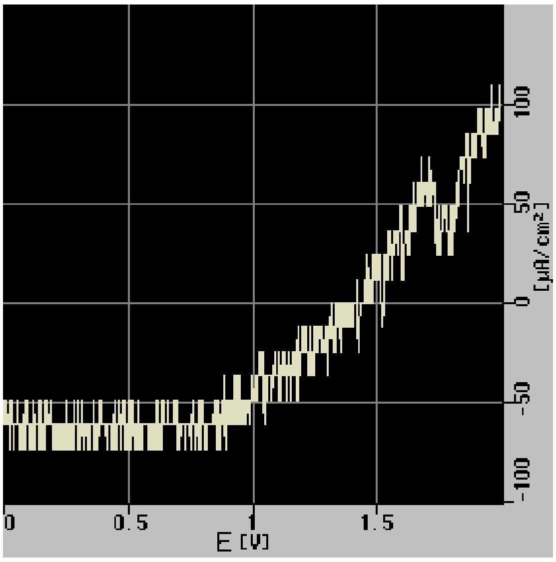


Figure 6 Polarization curve of TiN thin film coating (No.18)
in 3% NaCl aqueous solution at 297K.

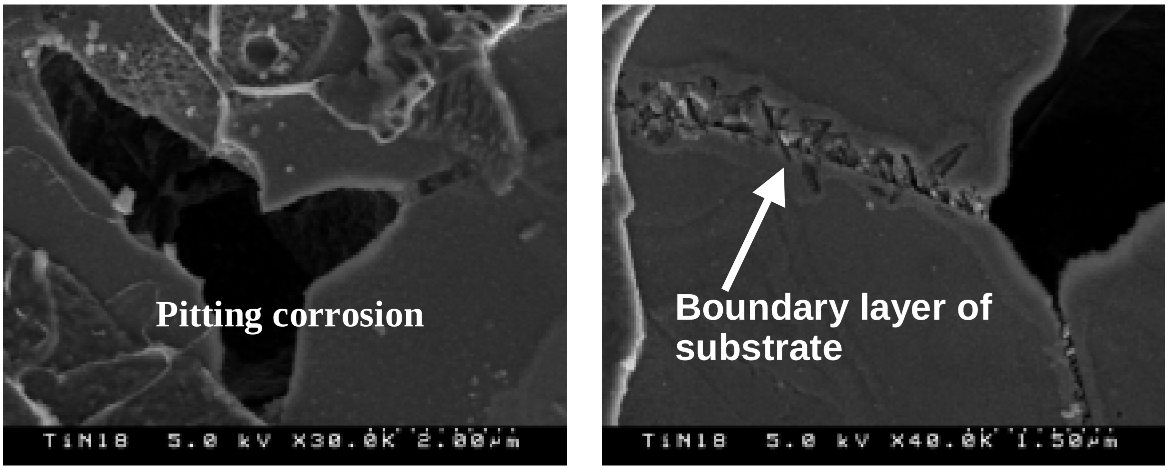


Figure 7 Surface morphology of TiN thin film coating (No.18) after corrosion test.

4. CONCLUSIONS

Localized corrosion behaviors of TiN thin film with different previous treatments were investigated employing Electrochemical AFM, FE-SEM and CCD. The results obtained were summarized as follows;
(1) By using Electrochemical AFM in situ observation, the localized corrosion process of TiN thin film in aqueous solution can be fully understood.
(2) TiN thin film coating No. 18 in which passive film of substrate was incompletely removed, showed inferior corrosion resistance due to exfoliation of thin film itself.
(3) Adhesive state of boundary layer between coated thin film and substrate was changed depend on previous treatment process. Localized corrosion behavior was also changed, depending upon the previous treatment.

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