Correlation between Localized Corrosion Morphology and the State of Interface of Coated TiN Thin Film

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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. In corrosive environment, these defects caused the problem of localized corrosion. Moreover, the evaluations of changes of structure and the state of interface between thin film and substrate which was brought about through employing different coating methods become extremely important. Therefore, TiN thin film coating used in this study was made by two different types of coating methods, that is, plasma CVD and Dynamic Ion Mixing (DIM), which have different interfacial strength. Then, defect morphology and nm or \( \mu \)m orders localized corrosion generated in 3\% NaCl aqueous solution was investigated by Atomic Force Microscopy (AFM). As a result, in TiN film coating made by the plasma CVD method, exfoliation of film itself was recognized from the initial stage. The crevice corrosion has been developed from this exfoliation. On the other hand, exfoliation of film itself was not confirmed in thin film coated by the DIM method. Therefore, differences in the initial state of film structure and the generated corrosion morphologies from those defects were observed. And also, improvements in corrosion and exfoliation resistances were recognized in case when superior adhesive state of interface between TiN thin film and substrate were realized.
1 Introduction

Ceramic coating made by vapor phase method was excellent in the high hardness, wear resistance, corrosion resistance. Therefore, ceramic coating was widely used as technique of thick and thin film formation to the various materials such as metals, ceramics, plastics. Also, a various thin film formation method was examined from the viewpoint of cost, and high function given to the substrate surface [1]. However, the great difference was generated in the mechanical and chemical characteristic of thin film coating due to the difference in previous treatment and ceramic film formation process. Especially, so far as the corrosion of thin film coatings is concerned, the governing factors were depended on the various film coating methods [2]. The ratio and distribution of defects generated in the film formation process, interfacial state between coated thin film and substrate and so on. 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. These corrosion damages are classified into almost three categories, that is, exfoliation of thin film itself, pitting corrosion of substrate and crevice corrosion in the boundary layer between film and substrate [3,4]. In this study, extremely initial stages of localized corrosion mechanism of two types coated TiN thin film in 3% NaCl aqueous solution were investigated by detailed observations of μm or nm orders using Atomic Force Microscope (AFM). Dynamic Ion Mixing (DIM) method and plasma CVD method were selected for TiN thin film coating method.

2 Experimental Procedure

Specimen used in this study was 0.5 μm thickness TiN thin film coated AISI304 stainless steel made by two different methods. One is Dynamic Ion Mixing (DIM) method that is expected to have superior adhesive strength between substrate and coating. Another is plasma CVD method which can be applied on all surface morphology including hole inside and so on. As coating temperature of plasma CVD method was relatively higher compared with other coating methods, TiN thin film coatings were controlled by the rate of titanium and nitrogen deposition. And also, chemical compositions of coating were examined by X-ray Photoelectron Spectroscopy (XPS) and the structure of coated layer was investigated by X-ray Diffraction.

The kind of defects and the surface morphologies of both TiN thin film coatings were observed by optical microscope and FE-SEM. Adhesive state between substrate and coated thin film was examined in detail by Scanning Ion Microscopy (SIM) with Focused Ion Beam (FIB) method, because of localized corrosion characteristics being extremely affected by these characters. For investigating the initial stages of localized corrosion process of coated TiN film, test specimen was freely corroded in 3 % NaCl aqueous solution at 303K during 20 hours. After immersion into 3 % NaCl aqueous solution during some duration, the specimen was took out from this solution and washed by water.
And also, the localized corrosion behaviors were investigated in detail by AFM in laboratory air atmosphere [5,6].

3 Experimental Results and Discussion

3.1 Types and morphology of defects in TiN thin film

In the plasma CVD coating, pinhole defect was confirmed through the observation made by optical microscopy and FE-SEM. Also, hillock defect was formed due to the difference of thermal expansion coefficient between TiN film and substrate. In case of TiN thin film coating made by DIM method, two types of defect, this is, pinhole and entrainment impurity dust defects were investigated by AFM. Figure 1 shows that the cracks on grain boundary of substrate and exfoliation of plasma CVD TiN thin film coating itself at initial stage were confirmed. From this figure, sensitization of substrate itself was caused in the process of plasma CVD coating under temperature condition of 973K. As a result, inferior adhesive strength of boundary layer between substrate and coated TiN thin film was recognized. Similar phenomenon was observed in pinhole defect on plasma CVD coated TiN thin film. On the other hand, in coated TiN thin film by DIM method, the cracks on grain boundary of substrate and exfoliation of TiN thin film coating itself were not recognized. SIM image of the cross section near entrainment impurity dust defect after dipped into 3%NaCl solution of 303K for 100 hours was shown figure 2. In this figure, crevice corrosion between coated thin film and substrate was not observed. Therefore, adhered state of boundary layer was improved by nitrogen ion bombardment.

![FE-SEM image of initial exfoliation TiN coating made by Plasma CVD method.](image-url)
Figure 2: SIM image of boundary layer on entrained impurity dust defect after 100 hours immersion into 3% NaCl aq. solution.

Figure 4: Exfoliation mechanism on pinhole defect in TiN thin film coated by plasma CVD method.
3.2 AFM investigation of localized corrosion mechanism

Localized corrosion process in hillock defect on plasma CVD coated TiN thin film was investigated and shown in figure 3. In this figure, partial exfoliation of hillock defect after 40 hours immersions was observed and shown in figure 3 (b). As a result, This process caused the substrate exposing to the solution, as shown in figure 1. Therefore, in case of plasma CVD coated TiN film, exfoliation of thin film itself was generated at about 10 μm sized hillock defect. Then, partial pinhole defects was generated. Finally, crevice corrosion was initiated at the boundary between thin film and substrate. This crevice grew up into macroscopic crevice corrosion of boundary layer between thin film and substrate. And also, grain boundary corrosion of substrate were generated. Localized corrosion mechanism concerning hillock and pinhole defects is shown in figure 4. On the other hand, in case of TiN thin film coating made by DIM method, localized corrosion at pinhole defect in coated TiN thin film after 160 hours immersions into 3 % NaCl aqueous solution was not recognized. However, localized corrosion generated in dust entrained defect on TiN thin film in case when coating was made by DIM method (figure 5). At first, micro-crack of about a few ten nm depth was generated in TiN thin film at entrainment impurity dust defects. Secondly, corrosion solution passed through TiN thin film into boundary between thin film and substrate. Then, localized corrosion was accelerated. Figure 6 shows the initial localized corrosion process on the dust entrained defect. From these result, the degradation of substrate and exfoliation TiN thin film itself in phase boundary between TiN thin film and substrate were occurred in plasma CVD coating made under temperature condition of 973K. Then, it is suggested that degradation from these defects are accelerated in case when corrosion environment become more severe. On the contrary, at pinhole defect on TiN film coating by DIM method, no exfoliation and no crack of TiN thin film itself and also no pitting corrosion of substrate were recognized in 3%NaCl aqueous solution. On the other hand, micro-cracks were formed on dust entrained defect in TiN thin film at first. Then pitting corrosion of substrate and crevice corrosion of boundary layer between TiN film and substrate were generated at this defect. As mentioned above, localized corrosion of TiN thin film coated by DIM method was restricted only on the dust entrained defect because of well adhesive state and improvement of substrate corrosion resistance. On the contrary, occurrence of crevice corrosion on TiN film made by plasma CVD method was generated due to its bad adhered state. Therefore, concerning with corrosion resisting characteristic of ceramic thin film coating, DIM method was recommended to selected as coating methods.
Figure 3: Morphology changes on the same defect by anodic dissolution.
Figure 5: Morphology changes on the same entrained dust defect by anodic dissolution.
Figure 6: Morphology changes on entrained dust defect in TiN thin film coated by DIM method by corrosion.

4 Conclusions

Localized corrosion morphology of TiN thin film made by two different coating methods were investigated employing AFM, FIB and FE-SEM. The results obtained were summarized as follows.

(1) In case of TiN thin film coating made by Plasma-CVD method, defects exit from initial stage in coating process bring about exfoliation of TiN thin film itself and micro-crack.

(2) In case of TiN thin film coating made by DIM method, micro-crack formation depend on immersion time into corrosive solution due to the corrosive media coming into generated nm order micro-crack.

(3) Initial surface and defects morphologies depend on coating method. And, degradation process depend on state of boundary layer between coated thin film and substrate.

References


