CORRELATION BETWEEN INTERFACIAL STATE OF PLASMA CVD COATED TiN FILM/SUBSTRATE AND PINHOLE DEFECT RATIO EVALUATION BY CPCD METHOD

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ABSTRACT

TiN-coated stainless steel prepared by plasma CVD has some difficulties in using for corrosion resistant film, because TiN films have various defects. From among these various defects in coated thin films, corrosion resistance of TiN film coated specimens was usually governed by pinhole defect. Therefore, for applying TiN film in corrosion surroundings, it is necessary to evaluate the existing state of defects in the film. The Critical Passivation Current Density (CPCD) method had some problems though this method could quantitatively estimate defects as a pinhole defect ratio R(%) through employing the values of the critical passivation current density of TiN thin film coated specimen i_{crit}(Coating/Substrate) and that of non-coated substrate specimen i_{crit}(Substrate). The most serious problem **is** the overestimation in defect ratio evaluation in the cases when large corrosion pits were generated and some parts of TiN films were exfoliated due to its low adhesion strength. The adhesion characteristic of TiN films, which was coated by plasma CVD, was investigated by the scratch test. Then, through investigating the relationship between temperature condition of TiN film formation and critical load of Lc obtained by scratch test, the adhesive strength between TiN film and substrate was evaluated. *Also*, through evaluating the substrate materials dependency upon adhesive strength, the applicable range of the CPCD test was made clear for the defect ratio evaluation of TiN films with various film thickness and adhesion strength. In addition, some improvements in CPCD test method for avoiding the overestimation of defect in film were discussed.

INTRODUCTION

Thin film coatings toward various types of materials such as metal and organic compound have been used for protecting substrate surface from harsh environment or adding a lot of functions to them[1]. However, nanometric defects and micro cracks were always existed in coated thin tilm from the initial stage. In actual environment, degradation was generated due to the penetration of the corrosive solution going into substrate through the nanometric defect of coating. Therefore, it is necessary to establish appropriate conditions for better thin film formation with fewer defects.

TiN coated stainless steel prepared by plasma CVD has some difficulties in using for corrosion resistant film, because TiN films have various defects. From among these various defects in coated thin films, corrosion resistance of TiN film coated specimens was usually governed by pinhole defect. Therefore, for applying TiN film in corrosion surroundings, it is necessary to evaluate the existing state of defects in the film. The Critical Passivation Current Density (CPCD) method[2]-[4] had some problems though this method could quantitatively estimate defects as a pinhole defect ratio R(%) through employing the values of the critical passivation current density of TiN thin film coated specimen i_{crit}(Coating/Substrate) and that of non-coated substrate specimen i_{crit}(Substrate). The most serious problem is the overestimation in defect ratio evaluation in the cases when large corrosion pits were generated and some parts of TiN films were exfoliated due to its low adhesion strength[5] and high residual stress.

Therefore in this study, the adhesion characteristic of TiN films, which was coated by plasma CVD, was investigated by the scratch test. Then, through investigating the relationship between temperature condition of TiN film formation and critical load of Lc obtained by scratch test, the adhesive strength between TiN film and substrate was evaluated. Also, through evaluating the substrate materials dependency upon adhesive strength, the applicable range of the CPCD test was made clear for the defect ratio evaluation of TiN films with various film thickness and adhesion strength.

In addition, some improvements in CPCD test method for avoiding the overestimation of defect in tilm are discussed.

EXPERIMENTAL PROCEDURES

Specimen

The specimen used in this study was 0.6~4.4μm thick TiN thin film specimen coated on **AISI** 304 and 440C stainless steels and **SKD** 61 by plasma CVD method. Table 1 showed conditions of film formation by plasma CVD method. 500°C and 900°C were mainly selected as the substrate temperatures for film formation. 2μm thick lilm coated specimen was prepared under each film formation conditions, and also for AISI 304 substrate 0.6μm , 1.5μm, 2.4μm and 4.4μm thick TiN film specimens were prepared. Then, the examinations of the crystal structure of deposited thin tilms were conducted by XRD.

Table 1 Conditions of TiN coating by plasma CVD

Pressure [Pa]		106.7
Substrate temperature [℃]		500 700 (AISI 304only) 900
RF power [W]		400
Gas flow [vol.%]	N_2	83.5
	H_2	13.0
	$TiCl_4$	3.5

Critical Passivation Current Density(CPCD) method

Specimen which can be applicable to this evaluation method is coated thin ceramic tilms with few μm thickness made by dry processes such as PVD and CVD.

Critical passivation current density i_{crit}[2]-[4] is measured in 0.5 mol / 1 - H_2SO_4 + 0.05 mol / 1 - KSCN aqueous solution of 25°C through sweeping potential from - 0.45 V to + 0.40 V(vs. Ag/AgCl, 3.33 mol/l-KCl) with sweep rate of 20 mV/min. Electrochemical measurement by three electrodes methods was conducted after deaeration treatment of KSCN solution more than one hour using N_2 gas. And then the defect ratio of thin film R[%] is evaluated from the following equation.

$$R = \frac{1}{fs} \times \frac{i_{crit}\ (\text{Coating/Substrate})}{i_{crit}\ (\text{Substrate})} \times 100[\%] \qquad (1)$$

Where, i_{crit}(Coating/Substrate) is the critical passivation current density of TiN thin film coated specimen and i_{crit}(Substrate) is that of non-coated substrate specimen. The value of the shape factor of corrosion pit fs is equivalent to 2, in case when the morphology of corrosion pit is semielliptical.

Scratch test

Scratch test was conducted under the conditions shown in Table 2 using scratch testing machine of Revetest made by Nanotech Co. Ltd. The critical load of LC for initiation of microdelamination of thin film obtained by scratch test was determined employing the JSME(Japan Society of Mechanical Engineers) Standard S 010-1996 "Standard Method for Evaluating the Defects in the Coatings Made by Dry Processings"[3]. The value of LC was synthetically evaluated from both the changes in friction load and AE counts and the morphology changes in scratch trace detected by microscopic observation.

Table 2 Conditions of scratch test

Indenter	Tip radius	200 μm
	Material	Diamond
Loading rate		100 N/min
Sliding rate of TP		10 mm/min
AE sensitivity		1.2

RESULTS AND DISCUSSIONS

Scratch test results

In Figures 1,3,6 and 7, diagrams of frictional force and AE counts changes depending upon vertical load were obtained by scratch test conducted by using various kinds of TiN films(substrate temperature:500℃-900℃, film thickness:1.5μm-2.4μm) formed on AISI 304 stainless steel substrate by CVD method. *Also,* surface morphologies of coated specimens after scratch test were shown in Figures 2,4 and 5. In this paper, the critical load of LC for the initiation

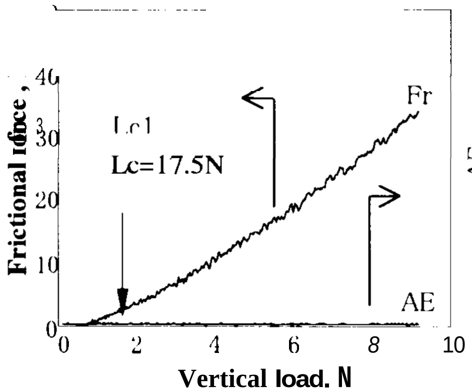

Figure 1 Results of scratch test of TiN/AISI 304 Substrate temperature:500℃, Film thickness:2.0μm

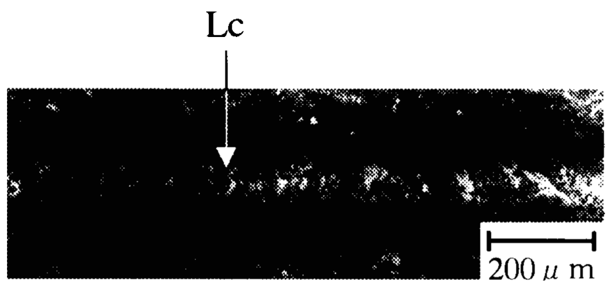

Figure 2 Surface morphology of TiN/AISI 304 after scratch test, Substrate temperature:500℃, 2.0μm

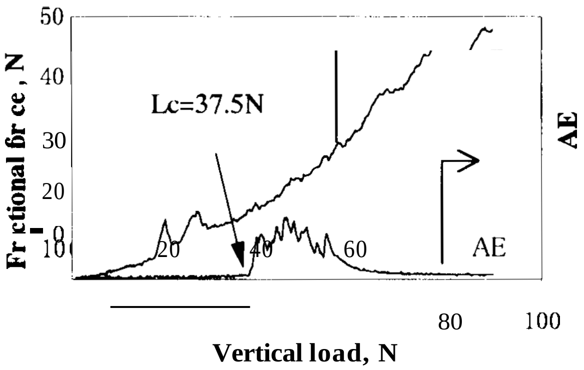

Figure 3 Result of scratch test of TiN/AISI 304 Substrate Temperature:700°C, Film thickness:1.5μm

Figure 4 Surface morphology of TiN/AISI304 after scratch test :700℃, 1.5μm

Figure 5 Surface morphology of TiN/AISI304 after scratch test :700℃, 1.5μm

of micro delamination was mainly determined by examining the morphological changes in the scratch trace observed by optical microscope. At the same time,AE count, and frictional force changes detected in the scratch test were **took** into consideration. In Table 2, conditions of scratch test, were indicated.

For 2.0μm thick TiN film coated at 500°C, the critical load LC **was** mainly determined by the scratch trace morphology change shown in Figure 2. The critical load Lc for 1.5μm thick TiN film made at substrate temperature 700°C was obtained to be 37.5N from the AE counts change shown in Figure 3. For 2.4μm thick TiN film made at substrate temperature 700°C, the critical load Lc was determined to be 36.8N(Figure 6) mainly considering the morphological change in scratch trace observed by optical microscope. *Also,* the critical load Lc for 2.0μm thick TiN film coated at 900°C **was** determined to be 50.4N(Figure 7) from the microscopic observation of morphological changes **of** scratch trace.

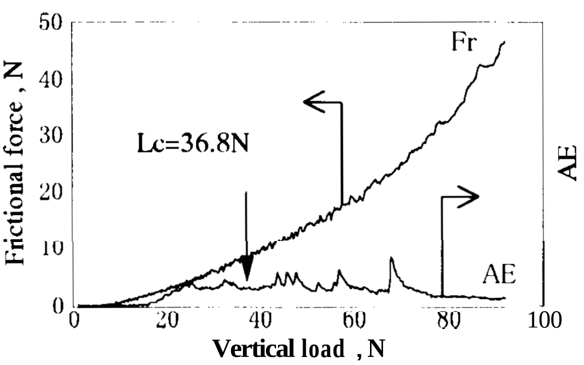

Figure 6 Result of scratch test of TiN/AISI 304 :700℃, 2.4μm

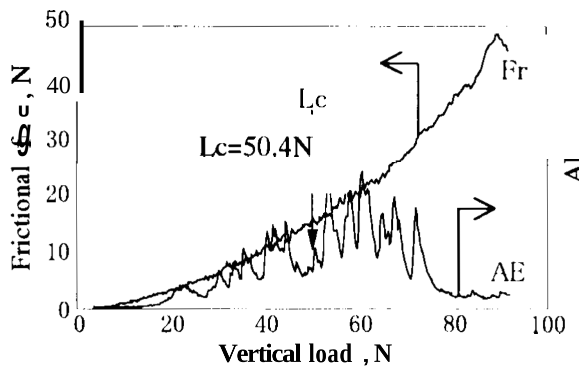

Figure 7 Result of scratch test of TiN/AISI 304 :900℃, 2.0μm

Employing the same test procedures scratch tests were conducted to determine the critical load LC for both TiN/AISI 440C stainless steel and TiN/SKD 61 coating systems. *Also* in these cases, the critical load **of** LC for the initiation of micro delamination was mainly determined by examining the morphological changes in the scratch trace observed by optical microscope. Obtained Lc data were shown in Table 3 together with the date for TiN/AISI 304 stainless steel substrate.

Table 3 The critical load Lc for the initiation of micro delamination obtained by scratch test

Substrate Temperature	Film thickness	Substrate materials		
		AISI 304	AISI 440c	**SKD** 61
500°C	2.0μm	17.5N	9.6N*	29.1 N
700°C	0.6μm	Not evaluated	------	------
	1.5μm	37.5 N	------	------
	2.0μm	Not evaluated	------	------
	2.4μm	36.8 N	------	------
	4.4μm	Not evaluated	------	------
900°C	2.0μm	50.4 **N**	57.7 N	*56.5* N

* The delamination morphology is different from other specimens

Dependency of the critical load Lc upon substrate material and substrate temperature

The critical load LC for the initiation of micro delamination increased with the increase of the substrate temperature in the film formation process. This means that the adhesion strength between TiN film/substrate increased with the increase of processing temperature of thin film formation. Under the film formation temperature 900℃, the Lc value of TiN coating becomes largest for **AISI** 440C stainless steel substrate. It decreases in the following order, i.e., TiN/AISI 440C, TiN/SKD 61 and TiN/AISI 304. The same tendency was also seen in TiN films formed at 500°C excepting **AISI** 440C substrate whose deformation morphology was different from other TiN/substrate systems.

The generation of hair crack was seen only in AISI304 substrate specimens, on the contrary, no cracks were generated both in AISI 440C stainless steel and **AKD** 61 substrate specimens. This implies that the generation of hair crack was dependent upon the hardness or the ability of plastic deformation of substrate materials. In fact, the hardness of these substrates material were detected by Vickers Indentation and obtained as 667[kgf/mm^2] for **AISI** 440C, 547[kgf/mm^2] for **SKD** 61 and 169[kgf/mm^2] for AISI 304 stainless steel, respectively.

Evaluation of Defect Ratio in TiN Coating Film by CPCD Method

The defect ratio R[%] of various types of TiN/substrate materials systems were evaluated by the Critical Passivation Current Density (CPCD) method and shown in Figure **8. As** mentioned before, the most serious problem is the overestimation in defect ratio evaluation in the cases when large corrosion pits were generated and some parts of TiN films were exfoliated due to its low adhesion strength and high residual stress[6]. Therefore, to examine the correspondence between the evaluated defect ratio by CPCD method and true defect ratio in TiN thin film, the initial defect ratio of 2.0μm thick TiN film coated on AISI 304, **AISI** 440C and **SKD** 61 substrates at 500℃ and 900°C was determined by the microscopic observation before electrochemical measurement. *Also*, the initial defect ratio of 1.5μm and 4.4μm thick TiN film coated on **AISI** 304 substrates at 700°C was determined by the microscopic observation before electrochemical measurement. From these result, only the obtained values of initial defect ratio of TiN/AISI 304 specimen coated at 700°C was shown also in this figure. The initial defect ratio of 2.0μm thick TiN film coated on AISI 304, AISI 440C and **SKD** 61 substrates at 500°C was obtained to be ranged about 0.9%-1.7% irrespective of substrate materials which was relatively large value. In contrast, the defect ratio R[%] evaluated by CPCD method was overestimated **to** be 35.1% for TiN film coated on **AISI** 304 substrate in which remarkable exfoliation was generated. The defect ratio R[%]

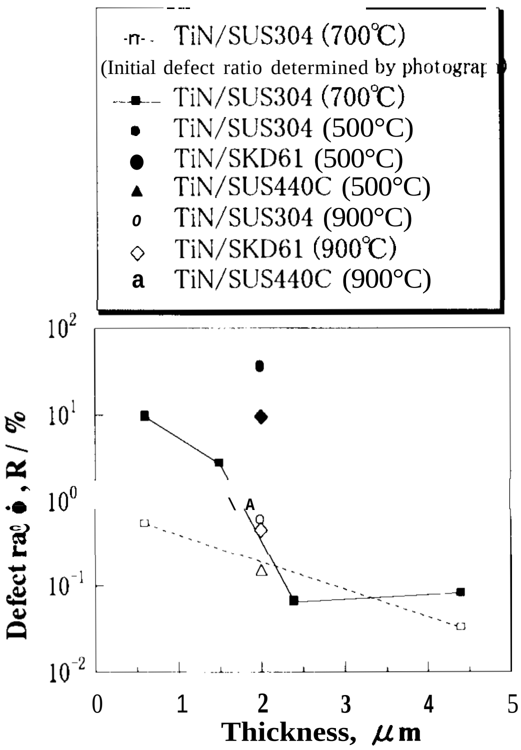

Figure 8 Relationship between TiN film thickness and defect ratio, in 0.5 mol/l-H_2SO_4 + 0.05mol/l-KSCN aq. Solu.

evaluated by CPCD method was also overestimated to be 9.44% for TiN/SKD 61 specimen in which large corrosion pits were generated compared with the initial defect size and some parts of TiN films were exfoliated. In the case of TiN/AISI440C specimen, the defect ratio R[%] evaluated by CPCD method was obtained to be 0.927% which was the smallest values in the specimens coated at 500°C instead of seeing some large sized corrosion pit and a little exfoliation in relatively small region. In this case, however, the defect ratio **R[%]** evaluated by CPCD method cannot be discussed with the adhesion characteristics of TiN film because the morphology of the exfoliation of this specimen was different from those of other substrate specimens.

Then, the initial defect ratio of 2.0μm thick TiN film coated at 900°C on AISI 304, **AISI** 440C and SKD 61 substrates obtained by the optical microscopic measurement was about 0.3% which correspond to TiN film with little defect. In these specimens, no remarkable generation of large corrosion pits and the exfoliation were seen after the CPCD test. The defect ratio R[%] evaluated by CPCD method method was 0.586% for TiN film coated on AISI 304 substrate. The defect ratio R[%] of TiN/AISI440C specimen was evaluated to be 0.144%, and that of TiN/SKD 61 specimen was obtained to be 0.448%. These evaluated values of R[%] were relatively small reflecting the higher adhesion strength between TiN coating and substrate metals. In fact, the critical load Lc for micro delamination of TiN films coated at 900°C showed relatively large values more than 50N. Therefore, no remarkable generation of large sized corrosion pit and the exfoliation were suppressed in this case. The superior correspondence between the defect ration R[%] determined by COCD method and the initial defect ratio detected by the microscopic observation was recognized. In this case, the defect ratio values determined by the CPCD test showed largest value for TiN/AISI 440C specimen, and that became the smallest for TiN/AISI 304 stainless steel specimen. These data were corresponded with the Lc values obtained by the scratch **test.**

The initial defect ration of 1.5μm and 4.4μm thick TiN films coated on **AISI** 304 stainless substrate at 700°C was determined by the microscopic observation before electrochemical measurement and shown in Figure **8.** The defect ratio values of TiN/AISI 304 specimens with 0.6 μm, 1.5μm, 2.4μm and 4.4μm thickness were evaluated by the CPCD method and shown also in this figure. The defect ratio R[%] of TiN/AISI specimens with 2.4μm and 4.4μm thickness determined by the CPCD method showed relatively good correspondence with the true defect ration obtained by the microscopic observation. Therefore, the CPCD method can be applicable to the defect ratio evaluation of these specimen with thickness larger than 2.4μm. In contrast, in the case of TiN/AISI 304 specimen whose film thickness was smaller than 2.0μm the defect ratio value R[%] determined by the CPCD method were overestimated as shown in Figure **8** compared with the true defect ratio 0.3%-0.5% determined by the microscopic observation due to the generation of large sized corrosion pit and the exfoliation of TiN film shown in Figure 9 whose mechanism was schematically shown in Figure 10. These defect ratio value R[%] were measured in 0.5 kmol / m^3 - H_2SO_4 + 0.05 kmol / m^3 - KSCN aqueous solution of 25℃ which was relatively severe environment for accelerating pitting corrosion at defect of TiN thin film.

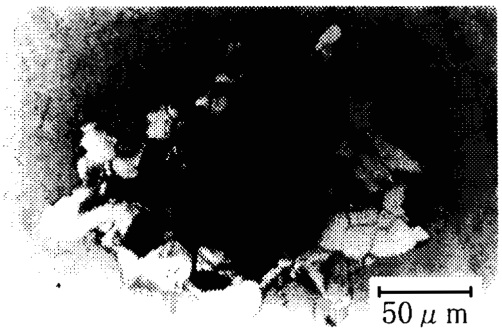

Figure 9 Surface morphology of TiN/SUS304 after CPCD test in 0.5 mol/l - H_2SO_4 + 0.05 mol/l − KSCN

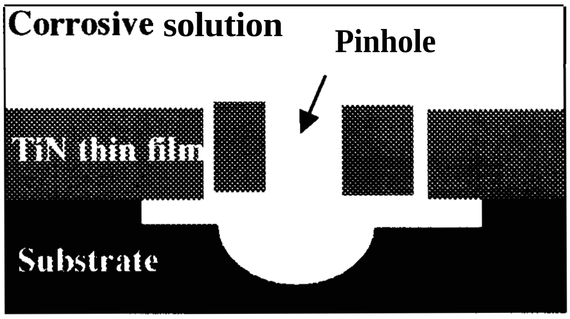

Figure 10 Schematic diagram of exfoliation of TiN thin film by corrosion damage in boundary.

Therefore, in the followings, The defect ratio evaluations for 0.6μm, 1.5μm thick TiN films coated on AISI 304 stainless substrate at 700°C were conducted in 0.5 mol / l - H_2SO_4 + 0.01 mol / l - KSCN aqueous solution of 25°C for suppressing the generation **of** large sized corrosion pit and the exfoliation of TiN film itself. *Also,* The defect ratio R[%] values for TiN films coated on AISI 304, TiN/AISI 440C and TiN/SKD 61 substrate at 500°C were evaluated in the same solution, and shown in Figure 11. The defect ratio for 1.5μm thick TiN films coated on AISI 304 stainless substrate at 700°C were obtained to be 0.953% which showed a little improvement in obtained result of the defect ratio through avoiding the exfoliation as shown in Figure 12 because of test being conducted in less severe corrosive solution. In contrast, in the case of TiN film whose thickness was 0.6μm, R[%] value was obtained to be 3.77% which showed a little improvement in the CPCD test result. In the case of TiN films coated on three kinds of substrate metals at 500°C the defect ratio data R[%] obtained in 0.5 mol / l - H_2SO_4 + 0.01 mol / 1 - KSCN aqueous solution of 25°C showed little improvement due to the inferior adhesive strength between TiN film and metal substrate. For these reasons, the CPCD method can not apply for the defect ratio evaluation of these TiN film coated at 500°C.

CONCLUSIONS

The adhesion characteristic of TiN films, which was coated by plasma CVD, was investigated by the scratch test. Then, through investigating the relationship between temperature condition **of** TiN film formation and critical load of Lc obtained by scratch test, the adhesive strength between TiN film and substrate was evaluated. *Also,* through evaluating the substrate materials dependency upon adhesive strength, the applicable range of the CPCD test was made clear for the defect ratio evaluation of TiN films with various film thickness and adhesion

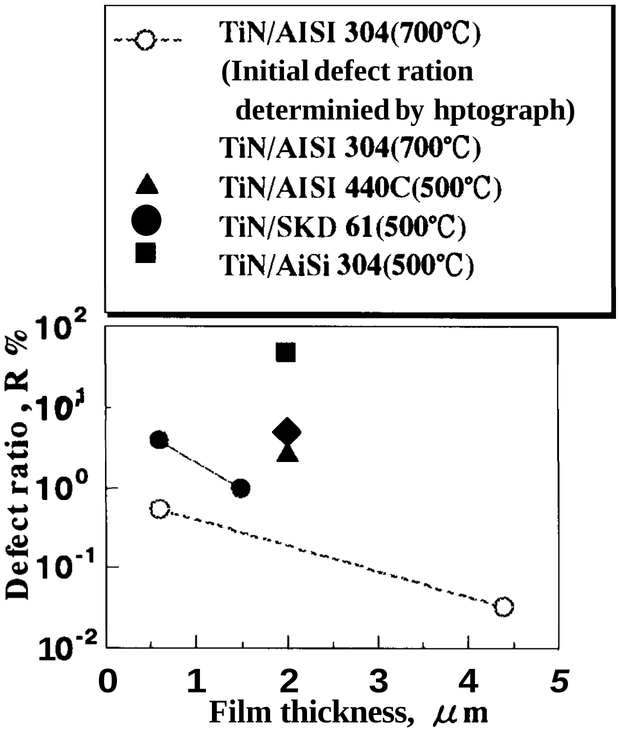

Figure 11 Relationship between thickness of TiN Films and defect ratio

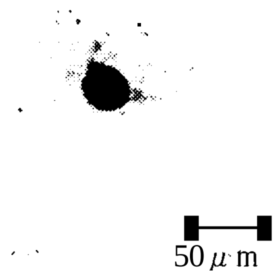

Figure 12 Surface morphology of TiN/SUS304 (700℃, 1.5 μm) after CPCD test in 0.5 mol/l · H_2SO_4 + 0.01mol/l-KSCN sol.

strength. In addition, some improvements in CPCD test method for avoiding the overestimation of defect in film are discussed.

Results obtained are summarized as follows;

(1) The adhesive strength between TiN coating and substrate metals is improved with the increase of substrate temperature of coating process.

(2) The CPCD method can be applicable to the defect ratio evaluation of the specimen with sufficient adhesive strength. Because of eliminating the generation of large sized corrosion pit and the exfoliation of TiN film.

(3) In the coated TiN films without sufficient adhesion strength, the evaluated defect ratio values R[%] by CPCD test are overestimated compared with the true defect ratio due to the exfoliation of TiN film itself.

(4) The defect ratio evaluation for **thin** TiN films showed a little improvement in obtained result through conducting the electrochemical test in less severe corrosive solution such as 0.5 kmol / m^3 - H_2SO_4 + 0.01 kmol / m^3 - KSCN aqueous solution.

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