Effects of Compressive Stress on Corrosion-Protective Quality and Its Maintenance under a Corrosive Environment for TiN Films Deposited by Reactive HCD Ion Plating*

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Titanium nitride films were deposited onto SUS304 substrates under various film thickness, deposition temperatures, and substrate bias voltages. Their protective quality was evaluated by electrochemical testing in accordance with the critical passivation current density (CPCD) method. Two types of tests were employed to evaluate corrosive behavior of coated substrates: a high-temperature and high-pressure corrosion test; and a measurement of the change in anodic current density with immersion time. A scanning electron microscope was used to examine surface morphology and fractured cross-sections of the films. Residual stress in the films was determined by the sin²θ method. An increase in film thickness engendered high protective quality. That protective quality was improved with increasing deposition temperature; micrometer-order pores were observed on all parts of films deposited at lower deposition temperatures, whereas few pores existed on films deposited at higher temperatures. This result indicates that these pores are one factor influencing overall protective quality. A film deposited with no substrate bias voltage displayed morphology with a typical columnar-structure; it also demonstrated complete protective quality. As the bias voltage increased, protective quality deteriorated, whereas an excess increase in the bias voltage gave rise to a slightly higher protective quality. Films with lower compressive stress had only a few pores and possessed higher protective quality, suggesting that pore formation originates in compressive stress. Corrosion tests indicated that the coated substrates corroded more rapidly as compressive stress in the film increased. The effect of compressive stress on maintenance of corrosion-protective quality was treated quantitatively. The rate of increase in the exposed area of film defects introduced in the films, which have a typical columnar-structure. Corrosion resistance of coated substrates is believed to be strongly related to the corrosion-protective quality of the films. Therefore, it is important to control process parameters to obtain high protective quality of the film. From such a perspective, relationships between protective quality and process parameters are reported frequently. Notwithstanding, very little information addresses essential factors that influence films’ protective quality, e.g. causes of through-film defect formation. Previous works have investigated effects of process parameters on hardness, chemical composition [N]/[Ti], impurity oxygen concentration, and residual stress for titanium nitride films deposited by reactive hollow cathode discharge (HCD) ion plating. This paper specifically addresses only the effects of film thickness, deposition temperature, and substrate bias voltage on the corrosion-protective quality of titanium nitride films. Based on these results, we will discuss factors influencing the protective quality and corrosion resistance of the coated substrates, and the maintenance performance of the protective quality under a corrosive environment.

1. Introduction

Hard coatings produced by the physical vapor deposition (PVD) method have been applied to increase tool life and to improve wear resistance of machine parts. Recently, hard coatings are also used to improve corrosion resistance of many steels because PVD methods allow deposition of ceramic materials which have stable chemical properties. Nevertheless, sufficient improvement in corrosion resistance of such coated steels is rarely obtained because of through-film defects introduced in the films, which have a typical columnar-structure. Corrosion resistance of coated substrates is believed to be strongly related to the corrosion-protective quality of the films. Therefore, it is important to control process parameters to obtain high protective quality of the film. From such a perspective, relationships between protective quality and process parameters are reported frequently. Notwithstanding, very little information addresses essential factors that influence films’ protective quality, e.g. causes of through-film defect formation.

Previous works have investigated effects of process parameters on hardness, chemical composition [N]/[Ti], impurity oxygen concentration, and residual stress for titanium nitride films deposited by reactive hollow cathode discharge (HCD) ion plating. This paper specifically addresses only the effects of film thickness, deposition temperature, and substrate bias voltage on the corrosion-protective quality of titanium nitride films. Based on these results, we will discuss factors influencing the protective quality and corrosion resistance of the coated substrates, and the maintenance performance of the protective quality under a corrosive environment.

2. Experimental

2.1 Reactive HCD ion plating

This study used an ion plating system: a model SHP-400T (Showa Shinku Co., Ltd.). Figure 1 shows a schematic representation of the system. The vacuum chamber is separated into evaporation and deposition chambers by a shutter. Heaters installed to the front, back, and upper sides of the deposition chamber are used to heat the substrate to a predetermined temperature. A hollow cathode is made of tantalum; the anode is a water-cooled copper hearth with a 14.5 cm³ capacity. The system is evacuated to a base pressure of 10⁻³ Pa.

A stainless steel plate (SUS304; 49 mm × 26 mm × 1.5 mm) served as the substrate. The substrate composition was analyzed and found to be: 0.05 mass% C, 0.39 mass% Si, 1.74 mass% Mn, 0.031 mass% P, 0.008 mass% S, 8.7 mass% Ni, 18.9 mass% Cr, 0.26 mass% Mo, and 0.79 mass% Cu. The substrate deposition surface was polished using diamond paste. The substrate was cleaned ultrasonically in acetone, n-hexane, and then acetone for 0.3 ks each before insertion into the ion plating system. Thereafter, Ar⁺ sputter cleaning for 0.9 ks was performed before film deposition.

We investigated effects of three deposition parameters: substrate bias electricity, deposition temperature, and substrate bias voltage. Table 1 shows ranges of these parameters.

Equivalent thickness of each film must be addressed to discuss corrosion-protective quality because the protective quality is largely dependent on film thickness. The substrate bias electricity was used to control film thickness accurately. Depositions were carried out by varying one parameter; the others were fixed at the standard values shown in the right column in Table 1. In subsequent discussion, the deposition condition using only standard values is called the “standard condition”.

### 2.2 Estimation of corrosion-protective quality of TiN films

Corrosion protective quality was examined by electrochemical tests in accordance with CPCD method, which is based on the assumption that critical passivation current density $i_{\text{crit}}$ obtained by measuring the anodic polarization curve for a coated substrate is proportional to the total exposed area of the substrate. We performed tests in an electrochemical cell comprising a working electrode designed to expose only $\phi 1 \times 10^{-2}$ m of the test specimen to the electrolyte while maintaining a sealed electrical contact with an O-ring made of Viton, a reference saturated Ag/AgCl electrode connected to the electrolyte by a salt bridge positioned at the surface of the test specimen, and a Pt plate (10 mm $\times$ 100 mm $\times$ 0.5 mm) as a counter electrode positioned on the side of the working electrode. The electrodes were separated with a glass filter. The electrolyte used was 0.5 kmol m$^{-3}$ H$_2$SO$_4$-0.05 kmol m$^{-3}$ KSCN, which was deoxidized by bubbling with N$_2$ at 4.17 $\times$ 10$^{-6}$ m$^3$/s for more than 3.6 ks before the test. The test temperature was 298 K. The polarization scan range was from $-450$ to $+400$ mV vs. Ag/AgCl; the polarization scan rate was 0.38 mV/s.

### 2.3 Corrosion tests

For a series of substrate bias voltage, evaluation of corrosion resistance was made using a high-temperature and high-pressure corrosion testing apparatus, model TAS-05 (Taiatsu Glass Kougyo Co., Ltd.), which is designed to estimate corrosion resistance of a plastic injection mold. Herein, this test is called the “high-temperature and high-pressure corrosion test”. Figure 2 shows a schematic diagram of the apparatus and the set of specimens used. The testing vessel is made of Hastelloy B$^{\text{TM}}$. The vessel is pressurized with compressed air; thereafter, it is heated to a predetermined temperature by a heater outside the vessel.

Coated substrates were exposed to gas generated through hydrolyzing $5 \times 10^{-2}$ kg of mixed resin (ABS:PVC = 7:3) at 433 K under 2.5 MPa pressure for 10.8 ks. It is presumed

![Fig. 1 Schematic representation of an HCD ion plating system.](image1)

**Table 1** Deposition parameters and their range applied to titanium nitride depositing.$^ {\text{a}}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate bias electricity, $Q$ (C)</td>
<td>60 $\sim$ 1200</td>
<td>480</td>
</tr>
<tr>
<td>Deposition temperature, $T_1$ (K)</td>
<td>330 $\sim$ 707</td>
<td>707</td>
</tr>
<tr>
<td>Substrate bias voltage, $V_B$ (V)</td>
<td>0 $\sim$ -90</td>
<td>-30</td>
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Electron beam current—180 A$^{\text{a}2}$; Total gas pressure—2.89 Pa; Gas mixture ratio N$_2$/(Ar+N$_2$)—0.925$^{\text{a}3}$; Distance between the substrate and evaporation source—242 mm.

$^ {\text{a}1}$Depositions were carried out by varying one parameter; the others were fixed at the values shown in the right column.

$^ {\text{a}2}$Electron beam voltages applied were 20–25 V.

$^ {\text{a}3}$Nitrogen partial pressure—2.67 Pa; Argon partial pressure—0.22 Pa.

![Fig. 2 Schematic representation of an apparatus used for high-temperature and high-pressure corrosion testing.](image2)
that gas, mainly composed of hydrogen chloride, is generated.\textsuperscript{17} The resultant condition was so harsh that wire SUS316 netting in the vessel often dissolved. Corrosion products were removed after the test by boiling in an 18 mass\%NaOH-3 mass\%KMnO$_4$ solution for 0.6 ks, in boiling water for 30 s, and then in a boiling 10 mass\%$(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ solution for 0.6 ks.

Furthermore, we measured the change in anodic current density at a potential with immersion time in the same electrolyte for the CPCD method to estimate corrosion progress of coated substrates. The test temperature was 298 K. A constant potential of $-200 \text{ mV vs. Ag/AgCl}$ was used.

2.4 Characterization of TiN films

Scanning electron microscopy (SEM) was used to examine film thickness as well as the films’ surface and fracture cross-sectional morphology. Phase and residual stress of the films were determined by X-ray diffraction using CuK$\alpha_1$ radiation. Conditions for residual stress measurement were proposed previously.\textsuperscript{11} We confirmed that all films were of single phase TiN.

3. Results

3.1 Effect of process parameters on corrosion-protective quality

3.1.1 Film thickness

Figure 3 shows the variation in $i_{\text{crit}}$ with film thickness $t_F$. Critical passivation current density $i_{\text{crit}}$ of the SUS304 substrate decreases remarkably by being coated with TiN films. As $t_F$ increases, $i_{\text{crit}}$ decreases abruptly at values up to $t_F \sim 2 \mu m$, but $i_{\text{crit}}$ decreases gently over $t_F \sim 2 \mu m$. This result indicates that an increase in thickness improves the corrosion-protective quality of the film. Kado \textit{et al.}\textsuperscript{12} reported that the logarithm of current density at a potential in anodic polarization curve of carbon steel, SS41, and stainless steel, SUS304, coated with TiN measured in 1 kmol$^{-1}$m$^{-3}$HCl decreased linearly with increasing thickness. This current density has been discussed as the value corresponding to corrosion-protective quality. Nevertheless, Fig. 3 shows a nonlinear relationship.

3.1.2 Deposition temperature

Figure 4 shows the variation in $i_{\text{crit}}$ with deposition temperature. As the temperature increases, $i_{\text{crit}}$ decreases, thereby improving the corrosion-protective quality of films. Tarutani \textit{et al.}\textsuperscript{6} have shown that $i_{\text{crit}}$ of SUS304 coated with TiN decreased with increasing substrate temperature; however, poor corrosion resistance was found over 773 K. This poor quality may result from sensitization of the substrate.\textsuperscript{18} No sensitization occurred for the substrate deposited at 707 K in the present study.

3.1.3 Substrate bias voltage

Figure 5 shows variation in $i_{\text{crit}}$ with substrate bias voltage $V_B$. As $|V_B|$ increases, $i_{\text{crit}}$ increases and reaches the maximum value at $V_B = -30 \text{ V}$; subsequently, it decreases. Although the $i_{\text{crit}}$ value at $V_B = 0 \text{ V}$ is high, the anodic polarization curve of this coated substrate differs entirely from the other curves, as shown in Fig. 6. Polarization curves of the substrate coated under applied bias voltages show anodic activation peaks just as that of the uncoated SUS304 substrate; on the contrary, no peak is shown in the curve of the substrate coated using no bias voltage. This curve closely approximates that of TiN film deposited onto a quartz substrate under the standard condition (see Table 1), and that of sintered TiN in 0.5 mol$^{-1}$dm$^{-3}$H$_2$SO$_4$ measured by Matsuda \textit{et al.}\textsuperscript{19} This result confirms the complete corrosion-protective quality of the film deposited at 0 V.

Considering the values of current densities $i$ of the uncoated SUS304 substrate and the substrate coated under applied bias voltages at the region of passive state of
SUS304, the values of \(i\) of the 0 V-coated substrate and TiN film deposited onto a quartz substrate are considerably high. Although similar high current density is also reported in the anodic polarization curves of TiN films in 1 kmol/m\(^3\) \(\text{H}_2\text{SO}_4\) measured by Yamaguchi et al.,\(^1\) details for this behavior remain unknown.

### 3.2 Corrosion resistance of TiN coated substrates

Figure 7 shows surface appearances of coated substrates for a series of substrate bias voltages after the high-temperature and high-pressure corrosion tests. Corrosion pores appear on films deposited at lower bias voltages. Corrosive damage increases with increasing bias voltage, whereas an excess increase in the bias voltage brings about higher corrosion resistance. Corrosion behavior of TiN coated steels in a non-oxidation acid proceeds because of removal of the film at the through-film defects by dissolution of the exposed part of the substrate, as described by Yamaguchi et al.\(^1\) We infer that substrate exposure occurs by removal of the film through dissolution of substrate because this testing environment contains hydrogen chloride.

The result in Fig. 7 is closely related to the change in \(i_{\text{crit}}\) with substrate bias voltage, as shown in Fig. 5. However, it seems that increasing the residual stress, namely the compressive stress, of the film changes the corrosion resistance for the worse, as can be seen from the values of compressive stress in Fig. 7. For example, all of the film disappears for −15 V-coated substrate with the largest stress in this series.

Figure 8 shows typical changes in anodic current density \(i_c\) of TiN coated substrates for a series of substrate bias voltage at −200 mV vs. Ag/AgCl with immersion time. For the −30 V-coated substrate, \(i_c\) increased remarkably in the initial stage of the measurement; on the contrary, the rates of increase in \(i_c\) for −5 V, −15 V, and −90 V are slightly lower. It is notable that current densities \(i_c\) for low bias voltages, e.g. −1 V and 0 V, vary within very low ranges. As mentioned above, an increase in current density with immersion time, shown in Fig. 8, implies an increased exposed area of the substrate. Typical surface appearances of the substrates after the measurement are shown in Fig. 9: for 0 V and −1 V-coated substrates, only a couple of corrosion pores occurred, whereas the corrosion pores were larger for −3 V (see Fig. 9). In contrast, large areas of the film were removed at other voltages (e.g. −90 V; see Fig. 9), and particularly for −30 V (see Fig. 9) at which all of the film was removed. These results correspond to changes in corrosion-protective quality with substrate bias voltage, as shown in Fig. 5. However, it is also considered that corrosion damage increases concomitant with compressive stress. For example, for the film deposited at 0 V and −1 V with low compressive stress, pores did not enlarge remarkably, showing no apparent relation to corro-
4. Discussion

4.1 Factors influencing corrosion-protective quality

4.1.1 Effect of columnar structure on corrosion-protective quality

Films deposited by the PVD methods normally have a columnar structure that does not usually exist in film bulk materials. For example, growth morphology of TiN films changes remarkably with varied substrate bias voltage.\(^8\) The SEM micrographs in Fig. 10 show the typical fracture cross-sectional morphology of TiN films deposited at various bias voltages. Growth morphology of the film deposited with no substrate bias voltage shows a typical columnar structure of a zone I structure according to the classification by Thornton;\(^20\) with increasing the bias voltage, the structure changes from a columnar structure to a densely packed zone T structure comprising fibrous grains. The zone I structure is a porous structure composed of tapered crystallites separated by voids, as reported by Thornton.\(^19\) Yamamoto et al.\(^2\) indicated that defects, such as voids, located at columnar grain boundaries should be through-film defects. However, in the present work, corrosion-protective quality for the films of dense structure, such as Fig. 10(f), is poor. In marked contrast, a typical columnar structure demonstrates good protective quality (see Fig. 10(a)). These results suggest that it is difficult to infer that defects such as voids located at columnar grain boundaries have direct and strong effects upon films’ corrosion-protective quality.

4.1.2 Defects influencing corrosion-protective quality

Figure 4 shows that increasing deposition temperature improves the corrosion-protective quality of films. Surface morphologies of films deposited at various deposition temperatures are shown in Fig. 11. Many defects, namely micrometer-order pores, are formed in the film deposited at 330 K (see Fig. 11(a)). Electron probe microanalysis (EPMA) revealed that some of these defects were open pores that expose the substrate. The number of the pores decreases as

<table>
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<tr>
<th>Substrate bias voltage [V]</th>
<th>0</th>
<th>−3</th>
<th>−15</th>
<th>−30</th>
<th>−90</th>
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Fig. 8 Anodic current density of TiN coated SUS304 substrates at −200 mV vs. Ag/AgCl (3.33 kmol·m\(^{-3}\) KCl) as a function of immersion time in a 0.5 kmol·m\(^{-3}\) H\(_2\)SO\(_4\)-0.05 kmol·m\(^{-3}\) KSCN solution at 298 K. \(V_b\) is the substrate bias voltage; \(\sigma\) represents residual stress.

Fig. 9 Surface appearances of specimens after anodic polarization measurement; testing area is \(\Phi_{10}\) mm.

Fig. 10 Typical SEM micrographs showing morphology of TiN films grown at various substrate bias voltages.
the deposition temperature increases. This change relates closely to the result of the protective quality obtained by the CPCD method, as shown in Fig. 4. Apparently, the corrosion-protective quality strongly depends on the open pores formed in the films, rather than on defects such as voids located at columnar grain boundaries.

### 4.1.3 Effect of compressive stress on open pore formation

Compressive stress is normally induced in the films deposited by ion plating methods. Such stress may form open pores because of removal of a film from the substrate at a weakly adhered part. Figure 12 shows variation in compressive stress with substrate bias voltage $V_B$. At low $|V_B|$, the stress is low: the maximum value of stress occurs at about $V_B = -15$ V. Thereafter, an excess increase in $|V_B|$ engenders lower stress. The variation shown in Fig. 12 is similar to the change in $i_{\text{crit}}$, with substrate bias voltage shown in Fig. 5, except that the voltage where the maximum stress is obtained is different from the voltage which induced the maximum $i_{\text{crit}}$. Variation in compressive stress with deposition temperature is shown in Fig. 13. As the deposition temperature increases, compressive stress increases at lower temperatures, but decreases at higher temperatures. This behavior differs from the result shown in Fig. 4. However, it is considered that relaxation of stress occurs because of formation of many open pores by worsened adhesion of films in the range of lower substrate temperature. Figure 14 shows the relationship between critical passivation current density $i_{\text{crit}}$ and compressive stress for two series of deposition temperatures $T_I$ and substrate bias voltages $V_B$. Except for the 0 V-coated substrate, critical passivation current density $i_{\text{crit}}$ becomes higher with higher compressive stress: in other words, films of higher compressive stress have many open pores, which cause lower protective quality. This

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**Fig. 11** Typical SEM micrographs showing surface appearances of TiN films deposited at various deposition temperatures.

**Fig. 12** Variations in residual stress with substrate bias voltage.

**Fig. 13** Variations in residual stress with deposition temperature.
result suggests that pore formation originates from compressive stress.

4.2 Effect of compressive stress on maintenance of corrosion-protective quality under a corrosive environment

As mentioned above, it was considered that compressive stress in the films influenced not only corrosion protective quality, but also corrosion resistance of coated substrates. This section presents quantitative examination of the relationship between compressive stress and maintenance of the corrosion-protective quality.

4.2.1 Estimation of corrosion rate for substrates with controlled film-stress

An attempt has been made to clarify the relationship between compressive stress and corrosion rate using substrates with controlled film-stress. Films were deposited simultaneously onto six sheets of substrate that were deformed using backing plates with six various radii of curvature. Figure 15 shows a schematic diagram of the setup used to deposit films onto these deformed substrates. The substrate material was stainless steel, (SUS304; 15 mm × 24 mm × 0.7 mm). Deposition was done at substrate bias voltage of −90 V under total gas pressure of 4.40 Pa (other chosen parameters are standard values; see Table 1); this condition was selected to reduce compressive stress generated in the films.11) By returning the substrates to a flat state after deposition, the films must possess similar properties aside from compressive stress. Figure 16 shows the variation in compressive stress of the films along with respective radii of curvature. Compressive stress increases with decreasing radius of curvature.

Changes in anodic current density $i_c$ of these substrates at −200 mV vs. Ag/AgCl in a 0.5 kmol·m$^{-3}$·H$_2$SO$_4$-0.05 kmol·m$^{-3}$·KSCN solution as a function of immersion time are shown in Fig. 17. Measurements were made up to $i_c = 100$ A/m$^2$ to prevent removal of the entire film from the substrate. An increase in compressive stress engenders a remarkable increase in $i_c$ and hence in the exposed area of the substrate. Figure 18 shows surface appearances of these substrates after measurement. The number of corrosion pores increases with increasing compressive stress; it is necessary for discussion of corrosion rate to take into account not only change in anodic current density $i_c$ but also the number of corrosion pores.

4.2.2 Quantitative treatment for the maintenance of corrosion-protective quality

This section presents quantitative treatment of the expansion rate of corrosion pores based on results in Figs. 17 and 18.
As shown in Fig. 18, corrosion pores are almost circular. We presume that the shape of initial through-film defects is circular. Let a radius of the number $i$ pore be $r_i$; then the initial total area $S_0$ of the exposed part of substrate is represented as

$$S_0 = \pi \sum_{i=1}^{n} r_i^2,$$  \hspace{1cm} (1)

where $n$ is the number of corrosion pores. The total exposed area of the substrate at time $t$ must be determined by considering the shape of corrosion pores. Figure 19 shows a cross-sectional view of a corrosion pore measured with a surface roughness tester. The corrosion pore shape can be regarded as conical. Therefore, using radius $r_i^t$ and depth $h_i^t$ of the number $i$ pore at time $t$, the exposed area $S_t$ of substrate is given as

$$S_t = \pi \sum_{i=1}^{n} r_i^t \left( r_i^t + h_i^t \right)^{0.5}.$$  \hspace{1cm} (2)

Figure 20 shows the relationship between average size and depth of corrosion pores measured with a laser microscope, which can be approximated by direct proportionality, i.e. a straight line like that drawn in Fig. 20. Substitution of $h_i^t = a r_i^t$ into eq. (2) gives

$$S_t = \pi \left( 1 + \alpha^2 \right)^{0.5} \sum_{i=1}^{n} r_i^t \left( r_i^t + a r_i^t \right)^{0.5},$$  \hspace{1cm} (3)

where $\alpha$ is constant. The current density $i_c$ is proportional to

$$i_c = C \pi (1 + \alpha^2)^{0.5} \sum_{i=1}^{n} r_i^2,$$  \hspace{1cm} (4)
where \( C \) is constant. Furthermore, changes in \( i_c \) can be approximated by a function of \( t^2 \) inferred from data plotted on a semilogarithmic graph, as shown in Fig. 17. Therefore, the radius of a corrosion pore is considered to be a function of \( t \). If the rate of increase of the radius is constant for all corrosion pores, then radius \( r_i \) of the number \( i \) pore at time \( t \) is represented by

\[
r_{ri} = Vt + r_{i0},
\]

where \( V \) is the rate of increase of the radius. Substitution of eqs. (5) and (1) into eq. (4) yields

\[
i_c = B\left(\frac{\pi n V^2 t^2}{2} + 2\pi Vt \sum_{i=1}^{n} r_{i0} + S_0\right),
\]

where \( B \) is constant. Therefore, the amount in proportion to the expansion rate \( V \) of corrosion pore can be calculated by the number \( n \) of initial defects and coefficient \( t^2 \) obtained from the regression equation of the measured \( i_c-t \) curve as follows:

In eq. (6), we assumed that the expansion rate for every corrosion pore was constant. Now we consider the expansion rate of a corrosion pore having the same exposed area. The coefficient of \( t^2 \), \( B\pi n V^2 \), was obtained from the regression equation of the of \( i_c-t \) curve; also, \( A = (B\pi n V^2)/n \) was calculated. Then \( V = \sqrt{A} \) is proportional to \( V \), or

\[
V \propto v = \sqrt{A}.
\]

Data up to \( i_c \) of 10 A/m² equivalent for 10% of the current density at the end of the measurement (see Fig. 17) were used to exclude the effect of combined pores. Therefore, the number \( n \) of initial defects was determined by counting corrosion pores which have a radius with more than \( (1 - 1/\sqrt{10})r_{max} \) with an optical microscope (\( r_{max} \) represents the radius of the largest pore in a substrate). Data of the region included in data of all the substrates, from \( 2 \times 10^{-2} \) to \( 4 \times 10^{-1} \) A/m² in \( i_c/n \), were used for the regression.

Figure 21 shows the relationship between compressive stress and \( v \) calculated in the manner mentioned above. The expansion rate of corrosion pores increases with increasing compressive stress. Increased compressive stress encourages the progress of corrosion in coated substrates.

### 4.3 Validity on estimation of corrosion-protective quality by the CPCD method

Haruna et al.\(^{22}\) pointed out that the CPCD method overestimates the area of the exposed substrate by through-films defects because potential sweep in the region of anodic activation may expand the through-film defects. This section presents discussion of the validity of estimation of protective quality by the CPCD method.

Sirato et al.\(^{23}\) reported that protective quality is overestimated. Removal of the film from the substrate at the through-film defects affects measurement by the CPCD method when adhesion of the film is bad. However, no part of removal of film or enlargement of open pores was observed in film deposited at the lowest deposition temperature of 303 K; the film would thereby possess poorest adhesion among films deposited in the present study.\(^{21}\) On the contrary, enlargement of open pores occurred in thin films.

Figure 22 shows SEM micrographs that display the appearance of open pores before and after measurement by the CPCD method. Defects in the film with thickness of 0.36 µm expand because of dissolution of the substrate upon measurement, as shown in Fig. 22(a). This result indicates that the protective quality evaluated by the CPCD method is underestimated for the thickness of 0.36 µm. Both expanded and non-expanded defects were observed for the film with 0.84 µm thickness. In contrast, non-expansion, that is, no change is shown in the appearance of defects in the film with thickness of 3.56 µm after measurement, even though the exposed substrate dissolves (see Fig. 22(b)). It can be concluded that corrosion-protective quality for films with thickness of 0.36 µm and 0.84 µm is underestimated in comparison to actual protective quality, whereas that for thicker films than those above, i.e. all films with standard thickness in this work, is good enough.

### 5. Conclusions

Corrosion-protective quality of TiN films is improved by increased film thickness and deposition temperature. At low bias voltages, the protective quality is good; increasing the bias voltage worsens the protective quality, whereas an excess increase in the bias voltage engenders slightly improved protective quality.

A film deposited with no substrate bias voltage typically has a columnar structure and a completely protective quality, but it has been reported that a film with a typical columnar structure has more through-film defects than that with a dense-looking structure. This study confirmed that the protective quality depends greatly on micrometer-order open pores formed in the film rather than micro defects, such as voids, located at columnar grain boundaries. We inferred that pore formation originated in compressive stress.

Corrosion tests indicated that corrosive damage progressed more rapidly as the compressive stress increased. The rate of increase in the substrate area exposed to electrolytes through the pores can be estimated quantitatively from a change in current density at a potential with immersion time. This study revealed that a decrease in compressive stress contributes
greatly to maintenance of protective quality.

REFERENCES


Fig. 22 Typical SEM micrographs showing appearances of defects before and after CPCD measurement.