

Corrosion Resistance and Corrosion Fatigue Strength of Carbon Steel Coated with Chromium Nitride by Multistage PVD Method*

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Chromium nitride (CrN) exhibits good corrosion resistance in addition to excellent electrical and mechanical properties. A decrease in the number of defects such as pinholes or voids formed during deposition is required for improvement of corrosion resistance and corrosion fatigue strength of coated materials. A multistage physical vapor deposition (PVD) method was proposed in order to fabricate dense thin-coating films. In an electrochemical anodic polarization test in aerated 2% H₂SO₄ solution, 0.37 wt% C steel that was coated with CrN thin film using the multistage PVD method showed better corrosion resistance than a specimen coated by a conventional method. This is due to a decrease in the number of small defects in the coating film deposited using the multistage PVD method. Evaluation of the corrosion fatigue strength of multistage-coated steel was performed by means of a cantilever-type rotating-bending fatigue test in 3% NaCl solution. The corrosion fatigue strength of multistage-coated steel was improved compared with that of the uncoated steel; however, the increase in fatigue strength was less in the multistage-coated specimen than in the specimen coated by the conventional method, contrary to the experimental results obtained from the anodic polarization test. It was pointed out that corrosion fatigue strength is dependent on not only the number of defects but also the shape of large defects in the coating film.

Key Words: Corrosion Fatigue, Corrosion, Surface Treatment, Coating, Electrochemistry, Anodic Polarization Curve, Physical Vapor Deposition, Chromium Nitride, Carbon Steel

1. Introduction

The fabrication of a thin ceramic layer on the surface of various engineering materials by a variety of techniques has received considerable attention in the past few years^{(1),(2)}. In many cases, the fatigue strength of metals under various kinds of environment has been improved by the deposition of hard thin-film coating. The authors have previously reported that the fatigue life of TiN- or CrN-coated steel increased

in air and in 3% NaCl solution compared with that of uncoated steel⁽³⁾⁻⁽⁷⁾. This is due to the fact that the coating film suppresses crack initiation in air and protects the substrate from its corrosive environment. It was also found that the improvement of corrosion fatigue strength depends on the thickness of coating film, because defects such as pores and pinholes are formed in the coating film during deposition. A decrease in the number of defects is required for improvement of corrosion resistance and corrosion fatigue strength of coated materials. Optimization of deposition conditions or stacking of multilayers of different kinds of film has been proposed in order to produce films suitable for use in practical engineering materials⁽⁸⁾⁻⁽¹³⁾.

In order to investigate the improvement of corrosion resistance and corrosion fatigue strength of ceramic-coated steel, attention was focused on CrN

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ceramic coating deposited on 0.37 wt% carbon steel using the multistage physical vapor deposition (PVD) method. This method was applied to the fabrication of dense thin-coating films to improve corrosion resistance of coated steel. Electrochemical anodic polarization curves were obtained to evaluate corrosion characteristics of the coated specimen and to obtain information on defect formation in the coating film. Also, corrosion fatigue tests were conducted in 3% NaCl solution to examine the effect of coating film and to inspect the efficiency of the multistage PVD method for improving corrosion fatigue strength.

2. Experimental Procedure

2.1 Testing material

The substrate material used in this study was carbon steel, JIS S35C, normalized at 1138 K for 30 min. The chemical composition (wt%) of this steel is 0.37 C, 0.24 Si, 0.77 Mn, 0.019 P, 0.023 S, 0.1 Cu, 0.2 N and 0.4 Cr. Specimens used for the fatigue test were smooth and hourglass-shaped with a minimum diameter of 8 mm, while those used for electrochemical measurement were square pillars of dimensions $15 \times 15 \times 20$ mm. The substrate surface machined after heat treatment was mechanically polished with emery paper up to grade # 1000 and subsequently electropolished to a depth of about 15 μm .

2.2 CrN coating process

CrN film was deposited onto the specimen surface using the multistage PVD method which deposits thin films repeatedly up to a specified film thickness. The hollow cathode discharge process was employed in a vacuum of 1×10^{-3} Torr to generate a glow discharge in nitrogen into which chromium was evaporated at a constant substrate temperature of 723K. After argon-ion bombardment was performed on the specimen surface, CrN was deposited for 20 min to a thickness of 1.5 μm . The coated specimen was exposed to air and argon-ion bombardment was performed on the coating film. Then CrN deposition was carried out under the same condition as mentioned above. The multistage PVD method was applied to obtain two coating films of different thicknesses: one is 3 μm -thick coating film that consists of two 1.5 μm -thick CrN film layers (hereafter referred to as multistage 3 μm); and the other is 5 μm thick coating film that consists of two 1.5 μm -thick layers and one 2.0 μm -thick layer of CrN film (hereafter referred to as multistage 5 μm). For comparison of deposition methods, coating films of 1.5, 3, 5 and 10 μm thickness were prepared at deposition times of 20, 50, 80 and 160 min, respectively, by a conventional method which involves continuous deposition to the desired film thickness (hereafter referred to as monostage). The

reasons for utilizing the multistage PVD method are to create an active surface for genesis of nuclei by argon-ion bombardment and to suppress formation of defects in coating film by restricting the continuous growth of columnar grains.

2.3 Evaluation of corrosion resistance

Measurement of potentiodynamic polarization curves was carried out in aerated 2% H_2SO_4 aqueous solution at 303 K. CrN-coated specimens were embedded in silicon resin and the area used as the working electrode was 8×8 mm^2 . Potentiodynamic polarization curves were obtained at a potential scan rate of 0.5 mV/s, starting from a free corrosion potential after immersion for 1800 s to +2.0 V. The potentials are reported with respect to a Ag-AgCl reference electrode.

2.4 Corrosion fatigue tests

Corrosion fatigue tests were performed in 3.0% NaCl aqueous solution using a cantilever-type rotating-bending fatigue machine which was operated at 1780 rpm (29.7 Hz). Saline solution controlled at 298 ± 2 K was continuously circulated in a plastic reservoir through the tank at a flow rate of about 32 ml/min. Following the immersion of a specimen in the saline solution for one hour, the corrosion fatigue test commenced.

3. Experimental Results

3.1 Corrosion resistance and evaluation of defects by potentiodynamic polarization measurement

3.1.1 Potentiodynamic polarization curves

Potentiodynamic polarization curves obtained from the 3 and 5 μm multistage-coated steel are shown in Fig. 1. Curves obtained from uncoated and 1.5, 3, 5 and 10 μm monostage-coated steel are also shown to facilitate discussion of the difference in corrosion resistance between coating methods. In the uncoated specimen, the current density increases with increasing potential and the curve shows an anodic peak. Then, the current density decreases rapidly with further increase in the potential and a passivated region appears, because of the creation of a passivated film on the specimen surface. On the other hand, polarization curves of CrN-coated specimens differ from that of the uncoated specimen and exhibit a dependence on coating film thickness. The anodic peak which was observed in the curve of the uncoated specimen was not observed in the curves of CrN-coated specimens. The current density in the plateau region of the coated specimens was about three to five orders of magnitude lower than that of the uncoated specimen, and was dependent on coating film thickness. No significant difference in corrosion potential (E_{corr}) was observed

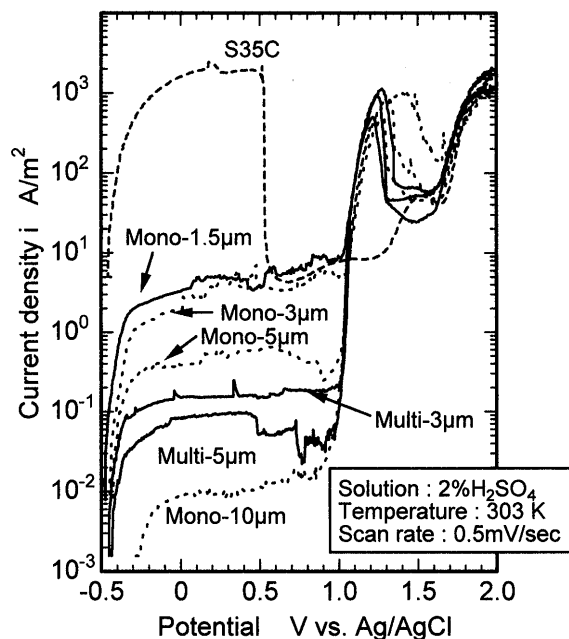


Fig. 1 Anodic polarization curves obtained from CrN-coated steel

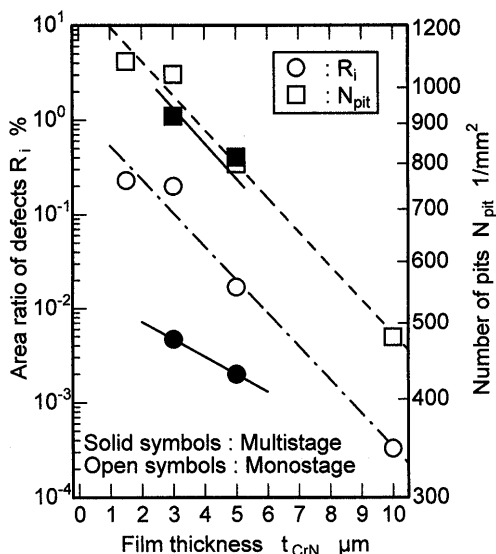


Fig. 2 Experimental relationship between area ratio, R_i , and number of pits, N_{pit} , of defect in coating film, and film thickness

between the multistage-coated specimens and the monostage-coated one at the same film thickness; however, the current density in the plateau region of multistage-coated specimen was lower than that of the monostage-coated one. From these results, it was found that coating using the multistage PVD method more effectively improves corrosion resistance compared with that using the conventional method.

3.1.2 Evaluation of defects Since CrN is electrochemically nobler than steel, the substrate area that is exposed to electrolyte via the pore openings acts as an anodic area and the measured corrosion

current indicates electrochemical dissolution of the exposed substrate areas beneath the pores. The critical passivation current density (CPCD) method proposed by Sugimoto⁽¹⁴⁾ was applied to the quantitative evaluation of defects in coating film in this study. The area ratio of defects in CrN film, R_i , is expressed as

$$R_i = \alpha \times \frac{i_{crit}(CrN/S35C)}{i_{crit}(S35C)} \times 100 \quad [\%] \quad (1)$$

where $i_{crit}(CrN/S35C)$ and $i_{crit}(S35C)$ are the critical passivation current densities of CrN-coated S35C and uncoated S35C steel, respectively, and α is a correction factor related to the shape of corrosion pits below a defect.

Figure 2 shows the relationship between film thickness, t_{CrN} , and area ratio of defects, R_i , calculated from Eq. (1). Since no anodic peak was found in the anodic polarization curves of CrN-coated steel, $i_{crit}(CrN/S35C)$ was determined at the potential of 0.3 V in this experiment. Also, α was assumed to be one-half because the corrosion pit formed on the substrate was hemispherical. The relationship between number of pits (pore openings) per unit area on the coating film, N_{pit} (1/mm²) measured by SEM, and t_{CrN} is also shown in this figure. Both R_i and N_{pit} decrease semi-logarithmically with increasing thickness of coating film. R_i of the multistage-coated specimen was about one-tenth that of the monostage-coated one.

3.1.3 Defect size distribution Defect size distribution was measured by SEM for specimens coated using the multistage and monostage PVD methods. The electrochemical test was interrupted at the potential of 0.3 V. Histograms of defect size distribution are shown in Figs. 3 and 4 by open bars. Most of the defects in the film are below 5 µm diameter and only a few are above 20 µm. It was clear that the number of small defects in the coating film deposited by the multistage PVD method was less than that in the film deposited by the monostage PVD method at the same coating film thickness. The number of large defects did not change with coating film thickness or coating method.

Figure 5 shows the defect size distribution in coating film plotted on a log-normal probability sheet. The defect size distribution shows approximately a log-normal distribution which does not change with coating method or coating film thickness.

3.2 Size distribution of defects formed during deposition

Quantitative evaluation of coating film defects using the CPCD method has shown that defects in the coating film that were formed during deposition expand, leading to coating film exfoliation from the substrate by dissolution during electrochemical

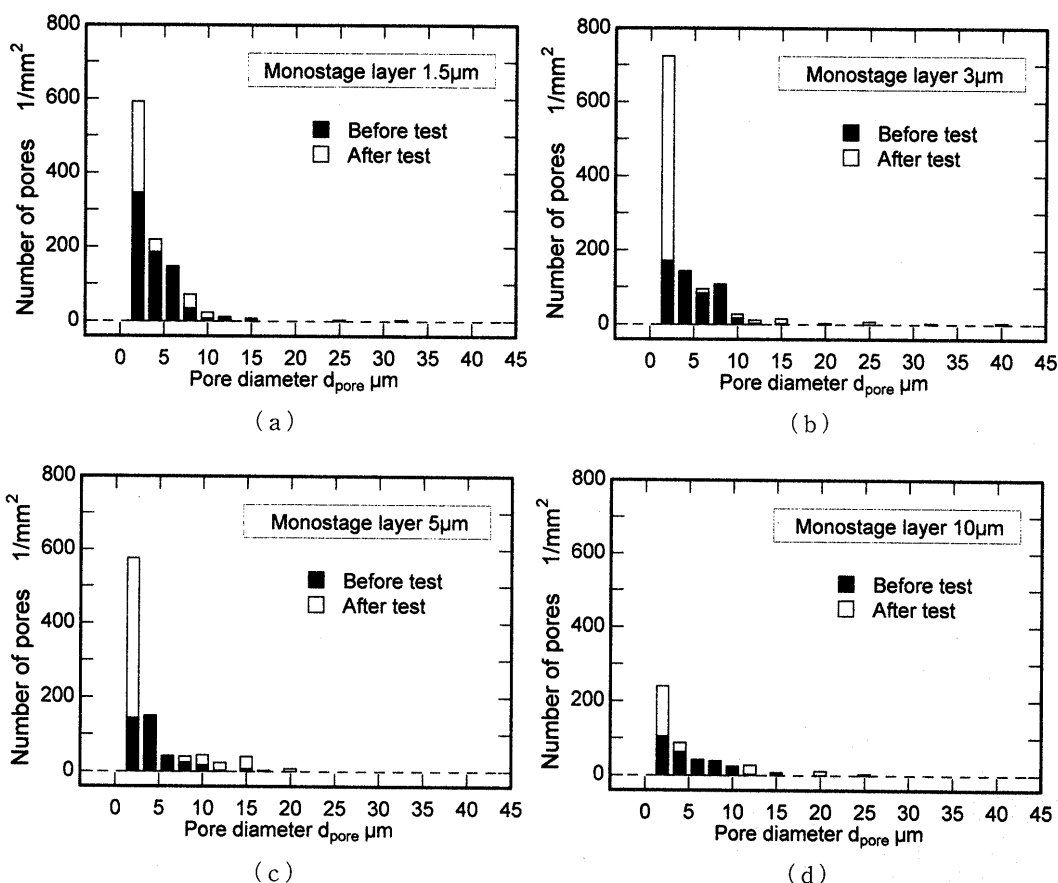


Fig. 3 Defect size distribution in coating film obtained using the monostage PVD method

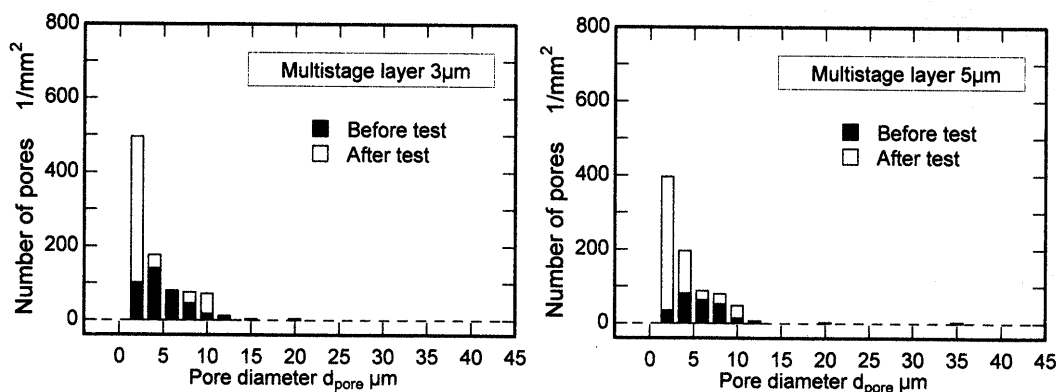


Fig. 4 Defect size distribution in coating film obtained using the multistage PVD method

polarization measurement⁽¹⁵⁾. It is necessary to understand the reason for the difference in defect size distribution before and after the anodic polarization test. To this end, size distribution of defects that were formed during deposition was measured by SEM and compared with the results in section 3.1.3.

Typical examples of surface defects in the coated specimen are shown in Fig. 6. Two kinds of defects were observed in the 3 and 5 μm multistage-coated specimens. One is a small pore that formed in a hollow (Fig. 6(b)) and the other is a large defect in a hollow that seems to be encapsulate, as shown in

Fig. 6(c) which is formed by multistage PVD. These pinhole defects show cone-like morphology. On the other hand, the pinhole defect in the 1.5 μm monostage-coated specimen has no hollow around it and shows a column-like shape (Fig. 6(a)).

Size distribution of surface defects formed during deposition, which was measured before anodic polarization test, is shown in Figs. 3 and 4 by solid bars. The number of small defects below 5 μm diameter decreased with increasing thickness of film deposited using both monostage and multistage PVD methods. However, the number of large defects above 20 μm

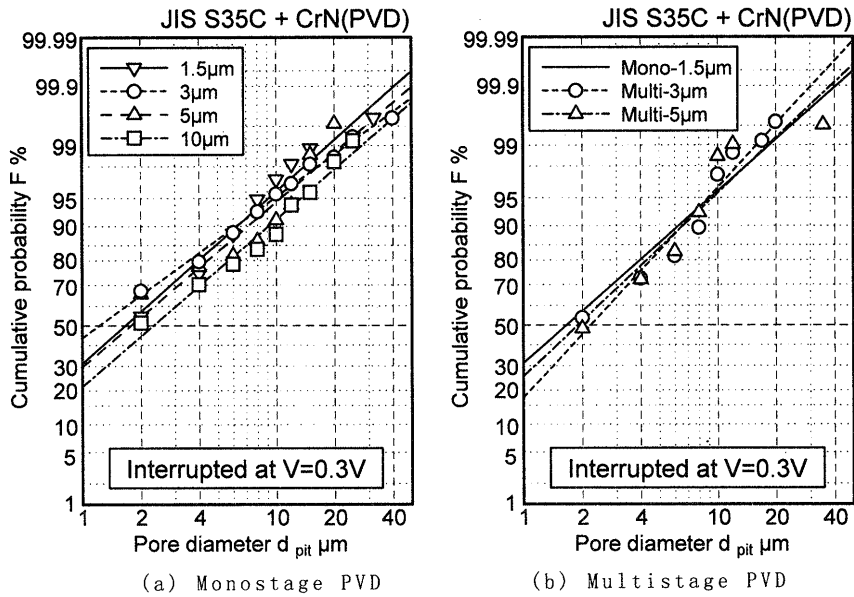


Fig. 5 Cumulative probability of defect size in coating film deposited by monostage and multistage PVD methods, plotted on a log-normal probability sheet

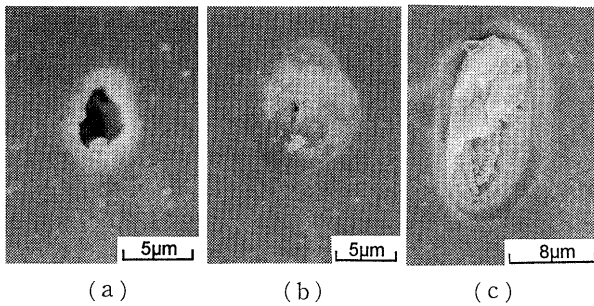


Fig. 6 SEM micrographs of defects in the coating film that were formed during deposition
(a) Monostage 1.5 μm , (b) Multistage 5 μm ,
(c) Multistage 5 μm

diameter did not change with the coating method or film thickness. It was clear that the number of small defects in the coating film deposited by the multistage PVD method was less than that in the film deposited by the monostage PVD method. The defect size distribution shows a log-normal distribution, similar to that obtained after anodic polarization test.

From a comparison of defect size distribution before and after anodic polarization test as shown in Figs. 3 and 4, the size and the number of defects after the test are larger than those before the test. This indicates that the coating film defects formed during deposition increase in size due to dissolution during electrochemical polarization measurement. The size and distribution of coating film defects are overestimated by the CPCD method.

3.3 Corrosion fatigue strength

3.3.1 S-N diagram Figure 7 shows the S-N curves of CrN-coated specimens obtained from the

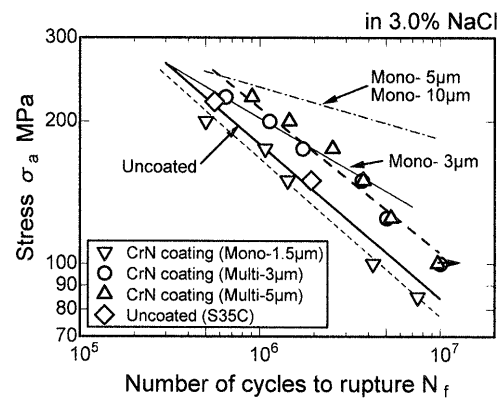


Fig. 7 S-N curves of CrN-coated steel obtained from the cantilever-type rotating-bending fatigue test in saline solution

corrosion fatigue test. S-N curves of uncoated and monostage-coated specimens are also shown for comparison. An improvement in corrosion fatigue strength is observed for CrN-coated specimens compared with the uncoated one, except for the 1.5 μm -thick monostage-coated specimen. No significant difference in corrosion fatigue strength is found between 3 μm - and 5 μm -thick multistage-coated specimens. At 10^7 cycles, the fatigue strength of multistage-coated specimen is 105 MPa, which is a 25% improvement over that of the uncoated specimen of 84 MPa. The improvement in corrosion fatigue strength is less in the specimens deposited using the multistage PVD method than that in those deposited using the monostage PVD method, contrary to the experimental result of corrosion resistance obtained from the anodic polarization test. This tendency is

obvious in the specimen with 1.5 μm -thick coating film.

Corrosion fatigue strength of the 1.5 μm -thick monostage-coated specimen was lower than that of the uncoated specimen. One of the authors⁽¹⁶⁾ has previously reported that the corrosion fatigue strength of TiN-coated steel with preflaws artificially induced in the coating film decreases compared with that of an uncoated specimen and a specimen with unflawed coating film, and the decrease depends on the preflaw density of the coating film. The reasons why corrosion fatigue life of the specimen with 1.5 μm -thick coating film is shorter than that of the uncoated specimen are that the substrate area that is exposed to saline solution via the pinholes acts as an anodic area and as a nucleus for the formation of corrosion pits, because CrN is electrochemically nobler than steels, and that there are many pinholes in the 1.5 μm -thick coating film.

3.3.2 Observation of fracture surface Macroscopic observations of the fracture surface of the specimens tested in saline solution revealed the presence of many ratchet marks on the fracture surface of uncoated specimen, which originated from multiple fatigue cracks, each of which produced a separate fatigue crack zone. Corrosion fatigue cracks propagate from small corrosion pits that have been formed by immersion in corrosive solution. This morphology is the same as that of coated specimens, although the number of ratchet marks on the fracture surface of the coated specimen is less than that of the uncoated specimen. The number of ratchet marks on the fracture surface of the 1.5 μm -thick monostage-coated specimen is less than that of the uncoated specimen and is inversely proportional to the corrosion fatigue life of the uncoated specimen. There is no difference in the number of ratchet marks on the fracture surface of monostage- and multistage-coated specimens.

Figure 8 shows an SEM micrograph of the corrosion fatigue crack initiation site on the fracture surface of the specimen deposited with 3 μm -thick coating film using the multistage PVD method. The corrosion pit was initiated on the metal substrate via the pinhole defect in the coating film, through which saline solution penetrated. Corrosion fatigue cracks of coated specimens were initiated at these corrosion pits and propagated. The corrosion fatigue crack initiation mechanism for specimens coated using the multistage PVD method is the same as that for uncoated specimens and specimens coated using the monostage PVD method.

Figure 9 shows optical micrographs of crack growth path on the fracture specimen surface. The corrosion fatigue crack of both monostage- and multi-

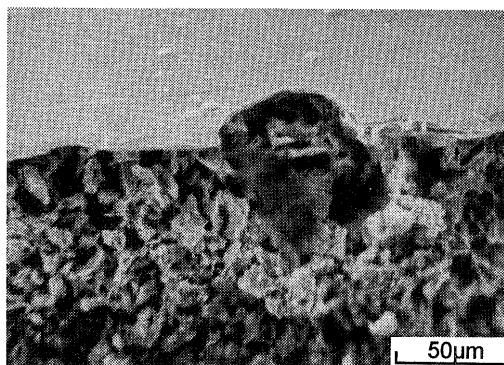
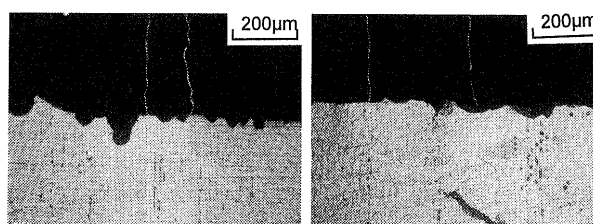


Fig. 8 SEM micrograph of corrosion fatigue crack initiation site on the fracture surface of the multistage-coated specimen (3 μm -thick coating film)



(a) Monostage, 1.5 μm -thick film (b) Multistage, 5 μm -thick film

Fig. 9 Optical micrographs of crack growth path on the fracture specimen surface

stage-coated specimens was initiated at a large corrosion pit and propagated independently via the small pits ahead of the crack tip. The crack also coalesced with cracks initiated at other corrosion pits. It can be seen that the irregularity of crack growth path on the surface of the specimen with 1.5 μm -thick coating film is larger than that of the specimen with 5 μm -thick coating film. This is due to the difference in the number of corrosion pits formed beneath the coating film, which corresponds to the number of pinhole defects in the coating film.

4. Discussions

In order to fabricate dense thin-coating film and to decrease the number of defects in the coating film, the multistage PVD method was proposed in this study. From evaluation with an electrochemical anodic polarization test, carbon steel coated using the multistage PVD method showed better corrosion resistance than that coated using a conventional method, because of a decrease in the number of small defects in the coating film. On the other hand, evaluation by corrosion fatigue tests indicated that the increase in fatigue strength was less in multistage-coated specimens than in specimens prepared using the conventional method, contrary to the results

obtained from the anodic polarization test. This suggests that the electrochemical anodic polarization test may be insufficient for evaluation of corrosion fatigue strength of coated steel. In this section, the reason for improvement of corrosion resistance by the multistage PVD method and the mechanism for controlling corrosion fatigue strength of coated steel will be discussed.

4.1 Improvement of corrosion resistance by multistage PVD method

The mechanism for reduction of the number of small defects in the coating film prepared by the multistage PVD method is schematically shown in Fig. 10. During the formation of coating thin-film by the PVD method, crystals grow perpendicular to the substrate surface and form columnar structures. Therefore, small defects are generated along grain boundaries. The continuous growth of defects that are formed during the first deposition process may be blocked during the second deposition process, because new nuclei are formed on the film surface activated by ion-bombardment and grains grow independently of previously formed grains. Thus the number of small defects reaching the substrate decrease with increasing number of deposited layers.

In attempts to control film microstructure and to decrease the number of defects in the film using several coating techniques, it was found that the multilayer coating method, which involves alternate stacking of different thin layers such as Ti/TiN⁽¹⁷⁾ or TiN/Cr₂N⁽¹³⁾, improved corrosion resistance. The multilayer coating method can reduce the number of defects, because of the formation of micro-granular structures in the TiN film and good adhesion of the film. From the experimental results mentioned above, we found it possible to fabricate dense thin-coating films and to improve corrosion resistance using the multistage PVD method, which involves repeated

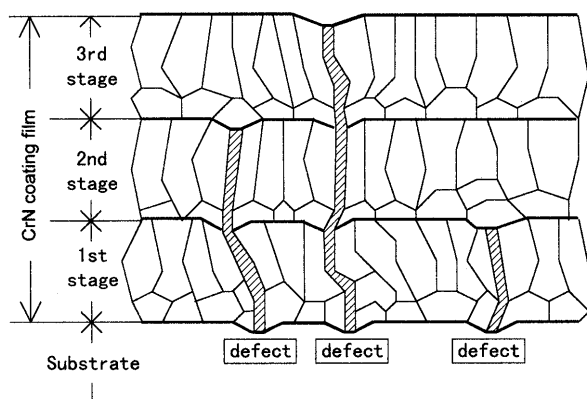
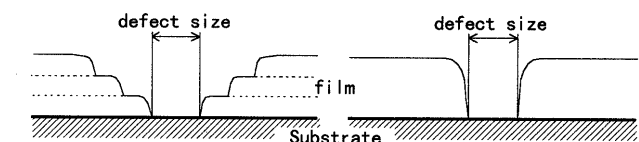


Fig. 10 Schematic of decrease in the number of small defects in coating film by the multistage PVD method

stacking of the same layer, in the same manner as the multilayer coating method. It is not clear which technique is superior in terms of reducing the number of defects in the coating film; however, the proposed method is easy to operate using conventional equipment compared with the multilayer coating method. Yamamoto et al.⁽¹⁷⁾ reported that the area fraction of defects decreased with increasing number of layers, and that maximum improvement was obtained for the 1.5 μm -thick coating film that consisted of eight layers of Ti and TiN stacked on a stainless steel substrate. In their study, the area fraction of defects changed from 0.1% for TiN single coating film to 0.02% for multilayer coating. In this study, the area fraction of defects of 0.1% for 3 μm monostage-coated film decreased to 0.005% for multistage-coated film. Therefore, it is expected that the multistage PVD method is more effective than the multilayer coating method for reducing coating film defects.

4.2 Corrosion fatigue strength and defects

In spite of the high corrosion resistance of specimens prepared using the multistage PVD method, based on the results of anodic polarization measurement, the increase in corrosion fatigue strength of the multistage-coated specimen was less than that in the monostage-coated specimen. The improvement in corrosion resistance of coated steel is necessary to protect the substrate from a corrosive environment, and is expected from the decrease in the number and area ratio of defects in the coating film. Corrosion fatigue strength, however cannot be accounted for by only the quality of corrosion resistance, because fatigue is controlled by localized damage. Corrosion fatigue crack of a coated specimen is initiated at a corrosion pit that is formed on the metal substrate due to penetration of saline solution through the pinhole defects in the coating film. A large corrosion pit will easily form below a large pinhole defect in the coating film via the galvanic action of local corrosion cells composed of the coating film (cathode) and the substrate (anode), and crack initiation at the pit occurs on the substrate at an early stage of the corrosion fatigue process. From the experimental results mentioned above, there was no difference in the size and number of large pinhole defects in the coating film deposited by the multistage and monostage PVD methods. Therefore, experimental results obtained from the corrosion fatigue test will be discussed with due consideration of two factors: one is the shape of large defects in the coating film on the specimen which influences corrosion pit formation and crack initiation during the corrosion fatigue process; and the other is crack growth behavior which is affected by the distribution of corrosion pits formed on the substrate below



(a) Multistage PVD method (b) Monostage PVD method

Fig. 11 Schematic of morphology of defect in coating film that was prepared using different deposition methods

the coating film.

In the multistage-coated film, the encapsulation, which corresponds to the number of depositions, was observed as shown in Fig.6(c), and manganese sulfide (MnS) was detected at the center of the hollow⁽¹⁸⁾. It is considered that in multistage PVD, the formation of a large pinhole defect in the coating film cannot be suppressed by subsequent deposition steps, and the pinhole defect has a cone-like shape, as shown in Fig. 11(a). On the other hand, in monostage PVD, a large pinhole defect that was formed during deposition increases in size continuously and becomes column-like, as shown in Fig. 11(b). It is predicted that saline solution penetration and exchange in the substrate via pinholes occur more easily in the cone-like defect than in the column-like one. Therefore, corrosion pit formation and crack initiation in the specimen coated using the multistage PVD method occur at an early stage of the corrosion fatigue process, compared with that coated using the monostage PVD method, even if the defect size of the specimens is the same.

A crack that is initiated at a corrosion pit propagates through other corrosion pits that are distributed ahead of the crack tip, and its growth is suppressed by blunting a crack tip as crack reached at corrosion pit. The retardation of crack growth may occur when the probability of the crack propagating through small corrosion pits during crack growth increases. From a comparison of the result shown in Fig.9(b) for multistage-coated with the results reported previously for monostage-coated specimen⁽⁵⁾, it was found that the number of corrosion pits along the crack growth path in the multistage-coated specimen was less than that in the monostage-coated one. This indicates the dependence of the number of small pinhole defects in the coating film. It is suggested that since the crack propagation rate of the multistage-coated specimen is faster than that of the monostage-coated one, corrosion fatigue life is shorter in the former. From the above discussion, it is found that the corrosion fatigue strength of the coated specimen depends not only on the evaluation of corrosion resistance by electrochemical anodic polarization test, but also on the number and distribution of pinhole defects in the

coating film.

5. Conclusions

In order to fabricate dense thin-coating films and to improve the corrosion resistance of coated steel, a multistage physical vapor deposition (PVD) method was proposed. Evaluation of corrosion resistance and corrosion fatigue strength in 0.37 wt%C steel coated with CrN thin film using the multistage PVD method was performed and the results were compared with those obtained from specimens that were fabricated using the conventional method. The following conclusions were obtained.

(1) From the anodic polarization test, the multistage-coated steel showed better corrosion resistance than the specimen coated using a conventional method.

(2) The improvement in corrosion resistance is due to a decrease in the number of small defects in the coating film deposited using the multistage PVD method.

(3) The corrosion fatigue strength of multistage-coated steel was improved compared with that of the uncoated steel; however, the increase in fatigue strength was less in the multistage-coated specimen than in the specimen coated by the conventional method, contrary to conclusion(1).

(4) It was pointed out that corrosion fatigue resistance was controlled by not only the number of pinhole defects but also the shape of large defects in the coating film.

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