Improvement in corrosion resistance of CrN coating steel with multi-stage deposition method and its corrosion fatigue strength
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Abstract

In order to obtain a dense thin coating film and improve corrosion resistance of coating steel, CrN thin film deposited on 0.37wt%C steel with multi-stage PVD method was studied. From an anodic polarization test in aerated 2% H$_2$SO$_4$ solution, the steel coated with the multi-stage method showed better corrosion resistance than the specimen coated with a common method. This is due to the decrease of small defects in the coating film by means of multi-stage deposition. Evaluation of corrosion fatigue strength on the multi-stage coating steel was performed under cantilever-type rotating bending fatigue test in 3% NaCl solution. From the experimental results, corrosion fatigue strength improved with the multi-stage coating as compared with those without coating. But an effort to improve corrosion fatigue strength was less in the multi-stage deposition than the common one, by contraries to the expectation of corrosion resistance obtained from the anodic polarization test.

1 Introduction

The production of thin layer of ceramics on the surface of various engineering components by a variety of techniques has received considerable attention in the past few years. In many interesting engineering applications of hard thin film coating, to improve the fatigue strength of metals under various kinds of environment is worthy of note. The authors have previously reported that fatigue life of CrN-coated steel increased in air and 3% saline solution as compared with that of uncoated steel[1]. This is due to the fact that CrN coating film protects the substrate from the corrosive environment. Also, it was found that the improvement of corrosion fatigue strength depends on thickness of coating film, because defects such as pore and pinhole are in the coating film produced during coating process. Decrease of these defects is required for
improvement in corrosion resistance and corrosion fatigue strength of coating materials. An optimizing of deposition condition or a stacking of multi-layer with different kind of film has been proposed by some researchers to get a valid film for practical engineering components.

In order to investigate the improvement of corrosion resistance and corrosion fatigue strength with ceramics coating, attention in this study was focused on CrN ceramics coating deposited on 0.37wt% carbon steel by physical vapor deposition (PVD). Multi-stage PVD method was proposed and applied to obtain a dense thin coating film and to improve corrosion resistance of coating steel. Electrochemical polarization curves were obtained to evaluate the corrosion characteristics of coating specimen and to get the information of defects in coating film. Also, corrosion fatigue tests were conducted in 3% saline solution to examine the effect of coating and to inspect an efficiency of multi-stage coating method for the improvement of fatigue strength.

2 Experimental Procedure

2.1 Testing material

The substrate material used in this study was 0.37wt.% carbon steel, JIS S35C, normalized at 1138K for 30 min. The chemical compositions (wt.%) of this steel is 0.37C, 0.24Si, 0.77Mn, 0.019P, 0.023S, 0.1Cu, 0.2N and 0.4Cr. Specimens used for fatigue test were hourglass-shaped smooth bar with minimum diameter of 8mm[1,2] and those used for electrochemical measurement were square pillar of 15×15×20mm. Substrate surface was mechanically polished with emery-paper (up to grade #1000) and subsequently electro-polished about 15μm thick.

2.2 CrN coating process

CrN film was deposited onto the specimen surface by multi-stage PVD method which is to deposit repeatedly thin film to a fixed film thickness. The hollow cathode discharge process was employed in vacuum of 1×10⁻³ Torr. to generate a glow discharge in nitrogen into which Cr was evaporated at a constant substrate temperature of 723K. After argon-ion bombardment was performed for the specimen, CrN was deposited for 20min to obtain the film thickness of 1.5μm. After that, the specimen was exposed in air and again argon-ion bombardment was treated for the coating film, and subsequently next CrN coating was carried out at same deposition condition. The multi-stage PVD method was applied to obtain the two different film thickness; one is 3μm thickness stacked 2 layers of each 1.5μm thick CrN film (referred as multi-stage 3μm), and the other is 5μm thickness stacked 2 layers of 1.5μm each and 1 layer of 2.0μm thick CrN film (referred as multi-stage 5μm). For comparison of deposition methods, film thickness of 1.5, 3, 5 and 10μm were prepared by different deposition time of 20, 50, 80 and 160min by the common deposition method which is to deposit continuously to a fixed film thickness (referred as mono-stage). The reason for introduction of the multi-stage PVD method was that to make the active surface for genesis of nuclei by an argon-ion bombardment and to obstruct the formation of defects in coating film by restrict
the continuous growth of columnar grains.

2.3 Evaluation of corrosion resistance

Measurement of the potentiodynamic polarization curve was carried out in an electrolyte of aerated 2%H₂SO₄ aqueous solution at 303K. CrN coated specimens were embedded in silicon resin and the area used as working electrode was 8x8mm². The potentiodynamic polarization curves were obtained with a potential scan rate of 0.5mV/s starting from a free corrosion potential after immersion for 1800s to +2.0V. 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 environment by using the cantilever-type rotating bending fatigue machine which operated at 1780rpm (29.7Hz). Saline solution controlled at 298±2K was continuously circulated in a plastic reservoir through the tank at a flow rate of about 32ml/min. Following the immersion of a specimen in the saline solution for one hour corrosion fatigue test was started.

3 Experimental Results

3.1 Evaluation of corrosion resistance

Potentiodynamic polarization curves obtained from the multi-stage 3 and 5μm coated steel were shown in Fig.1. In this figure, curves obtained from uncoated, 1.5, 3, 5 and 10μm mono-stage coated steel are also shown in order to discuss the effect of multi-stage method on corrosion resistance. In uncoated specimen, the current density increases with elevated potential and the curve presents an anodic peak. Following the anodic potential range, the current density decreases rapidly with increasing the potential and a passive region appears, because of creation of passive film on the specimen surface. On the other hands, polarization curves of the specimens with CrN coating are different from that of uncoated specimen and present a dependency on the thickness of coating film.
Anodic peak which presented in the curve of uncoated specimen did not present on the curves of CrN coated specimens. The current density of the specimen with coating at the plateau range was about three to five orders of magnitude lower than the value for the uncoated specimen and it depended on the film thickness. A significant difference of corrosion potential ($E_{corr}$) did not find between the multi-stage coated specimen and mono-stage one in same film thickness, but current density of multi-stage coating specimen at the plateau range was lower than the value for common one. From these results, it was clear that multi-stage method is more effective for improvement of the corrosion resistance as compared with the common one.

Specimen surface was observed by SEM after interrupted the electrochemical test at potential of $E=0.3\text{V}$. Some typical examples for the morphology of surface defects on coating specimen were shown in Fig.2. A lot of defects which have circular flaw of film were found in the mono-stage 1.5\text{\textmu m} coated specimen as shown in Fig.2(a). Two types of defects were observed in the multi-stage 3 and 5\text{\textmu m} coated specimens. That is, a small open pore formed in a hollow (Fig.2(b)) and a large corrosion pit grown by the dissolution of substrate. The morphology of these defects on the film was the same as that in the common coating method. On the other hand, it can be seen that there is shell-mark on the edge of a hollow which will be formed by multi-stage deposition method as shown in Fig.2(c).

Since CrN is electrochemically nobler than steels, the substrate area exposed to electrolyte through the open pores acts as the anodic area and corrosion current measured indicates the electrochemical dissolution of the substrate proceeded below the pores. The critical passivation current density (CPCD) method proposed by Sugimoto[3] was applied for the quantitative evaluation of surface defects in this study. An are ratio of surface defects, ($R_j$), in CrN film is given as:

$$R_j = \alpha \times \frac{i_{crit}(CrN/S35C)}{i_{crit}(S35C)} \times 100(\%)$$

where, $i_{crit}(CrN/S35C)$ and $i_{crit}(S35C)$ are the critical passivation current density of S35C coated with CrN and S35C steel respectively, and $\alpha$ is a

![Figure 2: Surface morphology of specimen with CrN coating by multi-stage method after corrosion test interrupted at potential of 0.3\text{V.}](image)
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Figure 3: Change in area ratio of defects and number of defects per unit area in coating film with thickness of CrN coating film.

Figure 4: Histograms of defect size distribution in CrN films by (a) mono-stage coating method, and (b) multi-stage coating method.

collection factor relating to the shape of corrosion pit under the defect. Figure 3 shows the relation between the film thickness $t_{\text{CrN}}$ and the area ratio of defects $R_j$ calculated from Eq.(1). Since the anodic dissolution peak can not be found on the curves in CrN coating steel the corrosion current density of $i_{\text{CrN}}(\text{CrN/S35C})$ was determined at the potential of 0.3V in this experimental condition. And also $\alpha$ is assumed as a half because corrosion pit formed in substrate was a hemisphere. Experimental relationship between number of defects (open pores) per unit area on the coating film, $N_{\text{pit}}(1/\text{mm}^2)$, and $t_{\text{crn}}$ are presented in this figure. It can be seen that the both $R_j$ and $N_{\text{pit}}$ decrease logarithmically with increasing the thickness of coating film. The $R_j$ of multi-stage coated specimen was about 10 times of magnitude lower than that of the common one.

3.2 Size distribution of defect

Size distribution of defects was obtained from the coated specimens interrupting the electrochemical test at the potential of 0.3V by the SEM observation and the results were shown in Fig.4. From this figure, it can be seen that the greater part of defects in the film is under 5$\mu$m diameter and a few was over 20$\mu$m. A number of small defects decreased, but a number of large defects did not changed with increasing the film thickness. As the result of comparison between Fig.4(a) and (b) at the same film thickness, number of small defects in the coating film deposited by multi-stage method was less than that by mono-stage method. This result corresponds to the area ratio of defects obtained from the anodic polarization curve.

The mechanism on reduction in number of defects by using the multi-stage coating method was shown in Fig.5. It is well known for the formation of thin
film by PVD method that crystals grow up perpendicular to the substrate and form columnar structure. Therefore, small defects occur along the grain boundary. Defects formed at the first deposition process may be blocked to continuous growth at the second deposition process, because that new nuclei of grains create on the active film surface by the treatment of ion-bombardment (see Fig.5(a) and (c)). Then the defects passed through substrate maybe decrease by multiple layers deposited. By the way, it was reported by one of the authors that large defect in coating film occurs at some defect, such as MnS, on substrate surface. It is considered that the large defect formed during deposition can not be stopped the growth by the following deposition process (Fig.5(b)).

3.3 Corrosion fatigue strength

Figure 6 shows the S-N diagram obtained from the CrN coating specimens under the corrosion fatigue tests. The S-N curves obtained from the specimen uncoated and coated by the mono-stage coating method are also shown in this figure. It can be seen from this figure that the improvement of corrosion fatigue strength is obtained in CrN coating specimens as compared with that of uncoated one, except 1.5µm thick coating specimen. And also, a significant difference of corrosion fatigue strength could not be found between 3 and 5µm coating specimen deposited by multi-stage method. These fatigue strength of $10^7$ cycles was 105MPa and an improvement was 25% for that of 84MPa on uncoated specimen. It is pointed out that an effort to improve the corrosion fatigue strength is less in the multi-stage coating method than the mono-stage one, by contraries to the expectation of corrosion resistance obtained from the anodic polarization test. Especially, corrosion fatigue strength of 1.5µm thick coating specimen was lower than that of uncoated specimen. One of the authors[2] has previously reported that the corrosion fatigue strength on TiN coating steel with preflaws induced artificially in the film decreases as compared with that of an uncoated specimen and one with unflawed coating film, and decrease the depends on the preflaw density in the coating film. The reason corrosion fatigue life in the specimen with 1.5µm thick coating film is shorter than that in the uncoated specimen is that the substrate area exposed to saline solution through the pinholes acts as an anodic area and a nucleus for the formation of corrosion pits, because CrN is electrochemically nobler than steels. Therefore, it is suggested that the incubation period prior to the formation of corrosion pits does not occur and crack initiation at the pit occurs on the substrate at an early stage of corrosion fatigue process in the specimen with

![Figure 5: Schematic illustration of the formation of defect during deposition process.](image-url)
4. Discussions

In spite of the efficiency for a corrosion resistance by the multi-stage coating method as the results of anodic polarization measurement, improvement in corrosion fatigue strength of multi-stage coating specimen was not enough as compared with that of mono-stage coating one. The improvement in corrosion resistance of coating steel is due to protect the substrate from a corrosive environment, and is expected by the decrease in number of defects and an area ratio of defects in coating film. But a corrosion fatigue strength can not explain by only the quality of corrosion resistance, because fatigue is controlled by the localized damage. The experimental results obtained in this study will be explained by the two factors; One is a shape of the largest defect in a coating film on the specimen which acts as a formation of corrosion pit and a crack initiation. The other is crack growth behavior which is affected by the distribution of corrosion pits formed on the substrate below coating layer.

Large defect in the film formed by the multi-stage coating process had a conical-like shape as shown in Fig.2(c), and that by the mono-stage one had a

Figure 6: S-N diagrams obtained under the corrosion fatigue tests in 3% saline solution.

Figure 7: Typical example of corrosion pit on the fracture surface beneath the coating film.

Figure 8: Macroscopic observation of the fracture surface tested under corrosion fatigue. (a) uncoated, and (b) multi-stage 5μm.
columnar-like shape (Fig. 5(b) and (d)). It is estimated that the penetration and exchange of saline solution into the substrate through pinhole are easier on a conical-like shape defect than on columnar-like one. Therefore, the corrosion pit formation and crack initiation of the specimen coated by multi-stage method occur at an early stage of corrosion fatigue process as compared with that coated by mono-stage method, even if the defect size is same with each other.

Figure 8 shows macroscopic observation of the fracture surface of the specimens tested under corrosion fatigue. Fracture surface observation of uncoated specimen revealed many ratchet marks which are the origins of multiple fatigue cracks. On the other hand, a few ratchet mark was observed on the fracture surface of the specimen coated by both multi- and mono-stage method. This means that a crack initiated at a corrosion pit propagates alone without coalescence. Crack growth will be affected by the corrosion pits which are in front of crack tip, and retarded by the blunting crack tip as crack reached at corrosion pit. The retardation of crack growth maybe occur easily under the condition of a uniform distribution of small corrosion pits in the substrate formed below the small pinholes in the coating film.

5 Conclusion

In order to obtain a dense thin coating film and improve the corrosion resistance of coating steel, CrN thin film deposited on 0.37wt%C steel with multi-stage PVD method was studied. The following conclusions were obtained.

(1) From an anodic polarization test, the steel coated with multi-stage method showed better corrosion resistance as compared with that coated with the common method.

(2) Improvement in corrosion resistance is due to the decrease of small defects in the coating film by the multi-stage deposition method.

(3) Corrosion fatigue strength of the multi-stage coating steel was improved as compared with that of uncoated steel, but an increase of fatigue strength was less in the multi-stage coating than in the common one.

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

References