

# An Ultrathin Corrosion-Resistant Film on a Steel Surface Formed by Dipping in a Tungstate Solution\*

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The surfaces of steel specimens after dipping in a solution with or without tungstate addition, followed by a corrosion test, were investigated by various techniques, e.g., cross-sectional Cs-(S)TEM, SEM and XPS, to gain an improved understanding of the role of tungstate in corrosion resistance. The corrosion reaction during the test was drastically suppressed when tungstate was added. A crystalline film approximately 4 nm thick consisting of Fe and O was formed on the surface after dipping in the solution without tungstate. After dipping in the solution with tungstate, a film consisting of Fe, O and W was formed with the thickness of about 4 nm. The latter film consisted of two layers; the outer layer showed lower crystallinity and a higher W concentration. This film improved corrosion resistance. It is supposed that (1) barrier properties are improved by the low crystalline layer or (2)  $W^{6+}$  in the film inhibits the corrosion reaction. The  $WO_4^{2-}$  in the solution also protected the surface during the test. When the ultrathin film is destroyed,  $WO_4^{2-}$  reacts with iron ions eluted from corrosion pits to form thicker protective films and pit propagation is also suppressed by segregation of  $W^{6+}$  in the corrosion products above pits.  
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## I. INTRODUCTION

Corrosion is one of the most important issues for steel products. Various kinds of inhibitors have been utilized to improve corrosion resistance in diverse ways. Inhibitors act in a corrosive solution and achieve improvement in corrosion resistance [1]. The mechanism of the effects of inhibitors has been extensively studied, mainly based on electrochemical approaches, resulting in an improved understanding of their electrochemical roles [2–5]. The structural change which occurs on the surface during the initial stage of corrosion is also important for understanding the mechanism; however, characterization of such ultrathin surface layers is difficult.

Oxoacids, which are known as typical inhibitors for steel products, suppress anodic (oxidation) and/or cathodic (reduction) reactions, thereby improving corrosion resistance. Tungstate, which is one oxoacids, inhibits anodic reaction by forming an ultrathin passivation film containing W on a steel surface in an acidic or a neutral solution [6, 7]. Although the elemental depth distributions and chemical states of the film have been revealed by surface analytical techniques, the morphology and crystallinity of the film have not been adequately investigated.

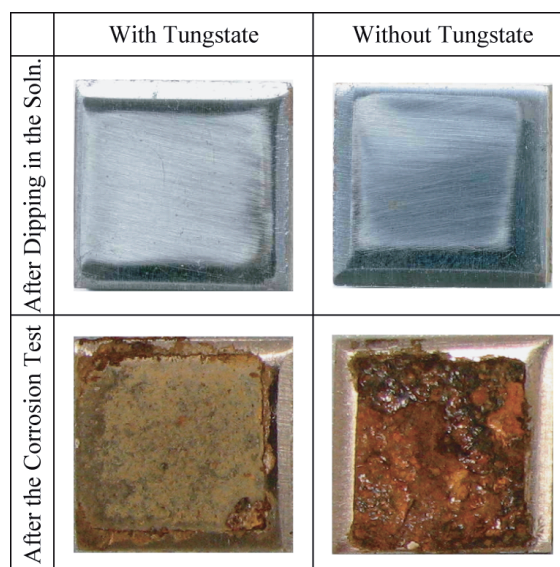


FIG. 1. Appearance of the steel platelets ( $15 \times 15 \text{ mm}^2$ ) after dipping in NaCl solutions with and without  $Na_2WO_4$  addition, followed by a corrosion test.

In this study, the surfaces of steel specimens after dipping in a solution with or without tungstate, followed by a corrosion test, were investigated by various techniques such as Cs-corrected (scanning) transmission electron microscopy (Cs-(S)TEM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The mechanism of the improvement in corrosion

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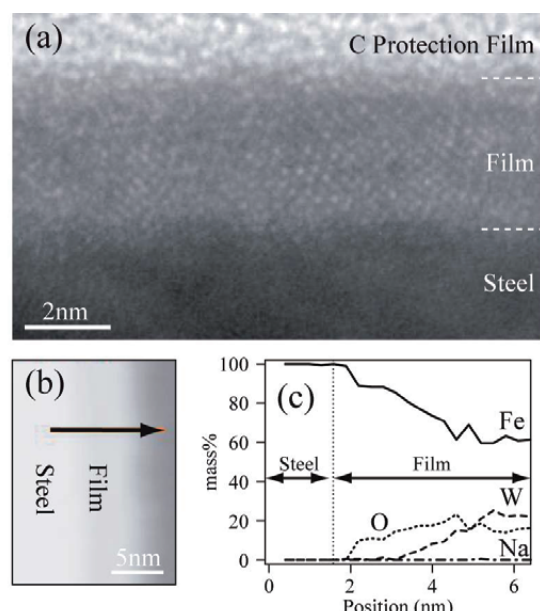


FIG. 2. Surface after dipping in the NaCl solution with  $\text{Na}_2\text{WO}_4$  addition. (a) Cross-sectional BF TEM image, (b) cross-sectional HAADF-STEM image and (c) STEM-EDS line profiles.  $E_P = 300$  keV. STEM observation and STEM-EDS line profile measurement were carried out at a different area near the area for TEM observation in the same lamella sample. The arrow in (b) indicates where the line profiles were measured.

resistance will be discussed based on the chemical states determined by XPS and the surface structures observed by Cs-(S)TEM and SEM.

## II. EXPERIMENTAL

The sample material used in this study was a low carbon steel sheet (2.9 mm thick) with W under the trace level. This material was cut into  $15 \times 15 \text{ mm}^2$  sized platelets, the surfaces were polished by emery paper (#400) and the back surface and edges were masked with protective tape. The samples were then dipped in a 5%-NaCl aqueous solution with or without addition of  $\text{Na}_2\text{WO}_4$  (0.3 mol/L) for 15 min at room temperature. Some samples were rinsed in distilled water after dipping and were used in characterization of the surface. The other samples were immediately moved to a corrosion test chamber in a wetted condition without rinsing after dipping and a corrosion test was performed under wet-dry cyclic conditions ( $35^\circ\text{C}$ -RH95% for 2 h  $\rightarrow$   $60^\circ\text{C}$ -RH30% for 4 h  $\rightarrow$   $50^\circ\text{C}$ -RH95% for 2 h) for 1 week. Subsequently, the samples were rinsed in distilled water before characterization.

The surfaces after only dipping and the corrosion test were investigated by (S)TEM (FEI Titan 80-300 or Philips CM 20 FEG) and SEM (LEO 1530). The cross-sectional samples for TEM and SEM observations were prepared by a focused ion-beam (FIB) milling apparatus (Hitachi FB-2000). The chemical states of the surface after dipping were investigated by XPS (SSI SSX-100). The X-ray source was monochromatized  $\text{Al K}\alpha$ , and the mea-

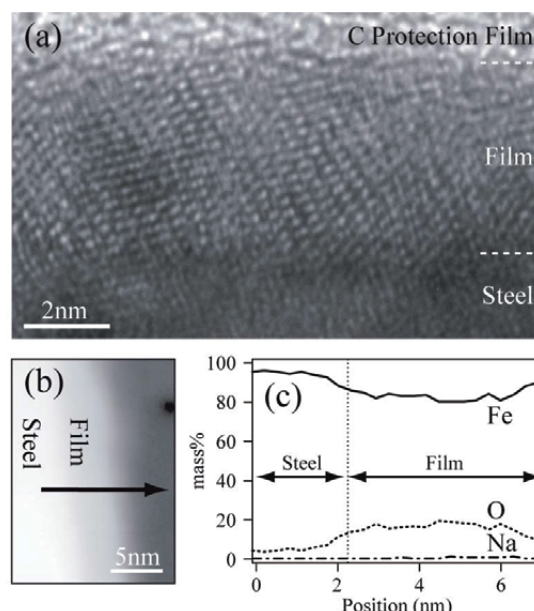


FIG. 3. Surface after dipping in the NaCl solution without  $\text{Na}_2\text{WO}_4$  addition. (a) Cross-sectional BF TEM image, (b) cross-sectional HAADF-STEM image and (c) STEM-EDS line profiles.  $E_P = 300$  keV. STEM observation and STEM-EDS line profile measurement were carried out at a different area near the area for TEM observation in the same lamella sample. The arrow in (b) indicates where the line profiles were measured.

surement area was 0.6 mm dia. Commercial reference materials of iron oxides, tungsten oxides and tungstates were also measured to estimate the chemical states of Fe and W on the surface. The reference materials were ground in an agate mortar, compressed onto In sheets and covered with Ni mesh to eliminate charging effects.

## III. RESULTS

### A. Appearance after Dipping and Corrosion Tests

Figure 1 shows the appearance of the steel platelets after dipping in the NaCl solutions with and without tungstate and the corrosion test. There were no significant differences between the samples after dipping; both surfaces showed a metallic cluster. However, addition of tungstate to the solution drastically improved corrosion resistance during the corrosion test. After the test, the surface without tungstate was completely covered with a thick rust layer. In contrast, the formation of rust was suppressed and some parts still retained their luster when tungstate was added to the solution.

### B. Surface Structure after Dipping in Solutions

In order to elucidate the mechanism of improvement in the corrosion resistance by tungstate, the surfaces after dipping in the solutions with and without tungstate were characterized.

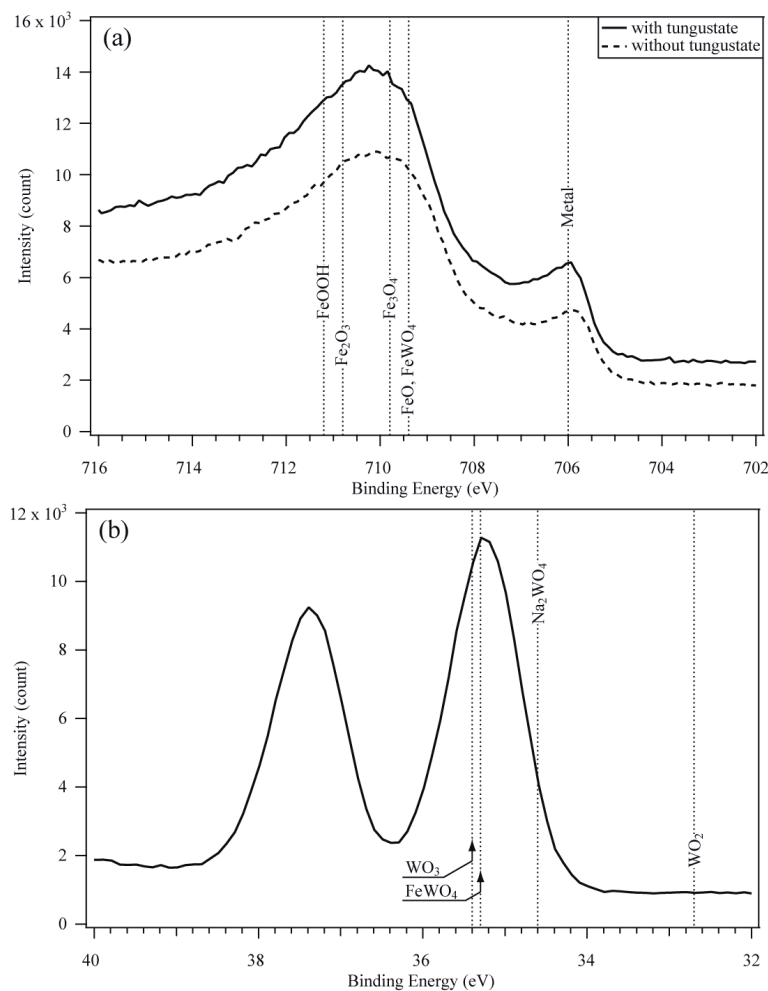


FIG. 4. XPS spectra of (a) Fe  $2p_{3/2}$  and (b) W  $4f$  of surfaces after dipping in the solutions with and without tungstate. Dotted lines indicate the peak positions of the reference materials.

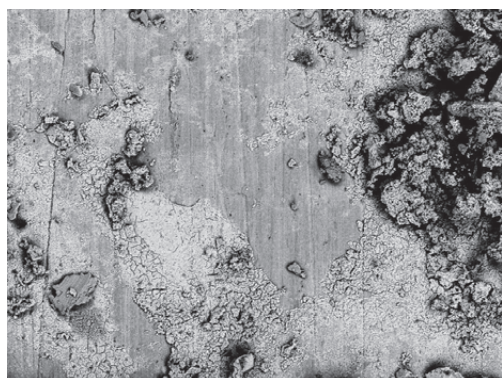


FIG. 5. Plane view BSE image of the surface with tungstate addition after the corrosion test.  $E_P = 5$  keV. The surface was categorized into following three areas as indicated in the image; the area where no film seemed to be formed (A), the areas covered with cracked films (B) and corrosion products (C).

Figure 2 and Fig. 3 show (a) cross-sectional bright-field (BF) TEM and (b) high-angle annular dark field (HAADF)-STEM images and (c) STEM energy dispersive X-ray spectroscopy (EDS) line profiles for the sam-

ples after dipping by FEI Titan 80-300. The STEM-EDS line profiles were measured along the arrows indicated in Fig. 2(b) and Fig. 3(b) in order to unveil elemental distribution near the surfaces. STEM observations and STEM-EDS line profile measurements were carried out at different areas near the areas for TEM observations in the same lamella samples. In both cases, ultrathin films approximately 4 nm thick were observed on the surfaces. However, differences were found in the crystallinity and composition of the films. Without tungstate, homogeneous lattice stripes were observed in the film, as shown in Fig. 3(a), while this feature gradually became unclear toward the top surface when tungstate was added, as shown in Fig. 2(a). As shown in the line-profiles in Fig. 2(c), the film formed with tungstate addition mainly consisted of Fe, W and O. The concentration of W gradually increased toward the top surface, and the atomic ratio W/Fe was estimated to be about 0.11 at the top part of the surface. In contrast, the film formed without tungstate mainly consisted of Fe and O, as shown Fig. 3(c).

Analysis of the chemical states of Fe and W on both surfaces was performed by XPS to understand the mechanism. Figure 4 shows the XPS spectra of Fe  $2p_{3/2}$  and W  $4f$  of the surfaces after dipping. The dotted lines indicate the peak energies of the reference materials. The binding

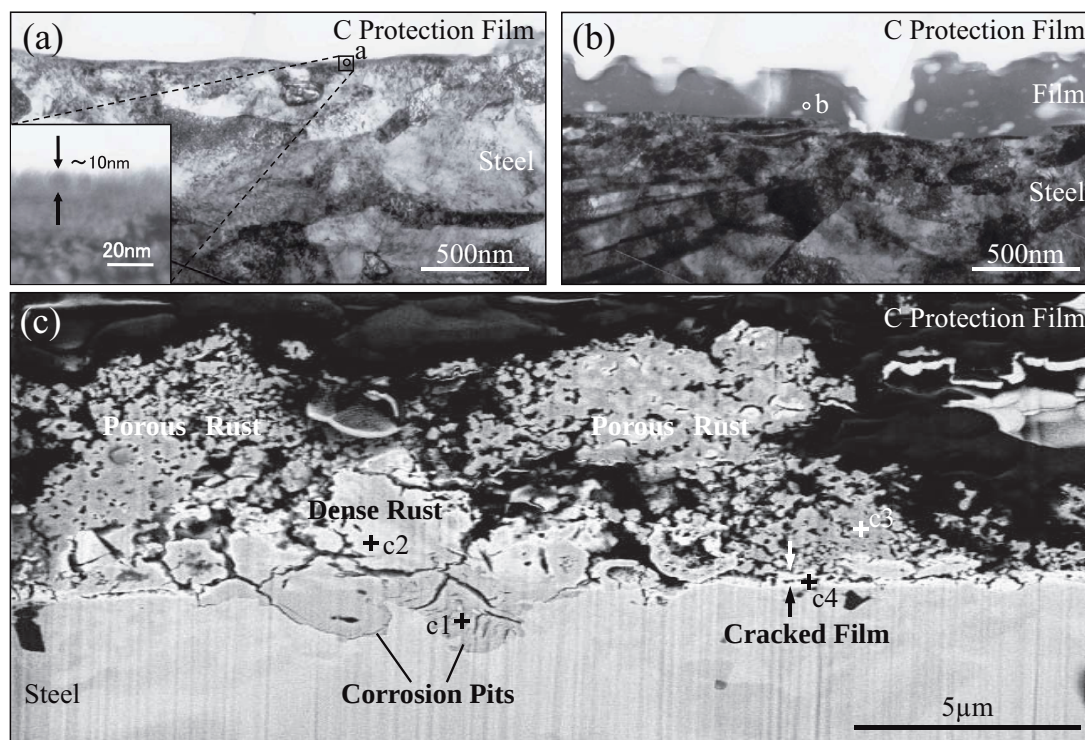


FIG. 6. Cross-sectional TEM and BSE images of the surface with tungstate addition after the corrosion test. (a) and (b) are BF TEM images at areas A and B, respectively ( $E_P = 200$  keV). (c) BSE image taken at area C ( $E_P = 5$  keV). The inset in (a) is an enlarged image of the near the surface region which is indicated by a square frame in (c). Circles and cross marks indicate areas where EDS spectra shown in Fig. 7 were measured.

energies of the main peaks of Fe  $2p_{3/2}$  on the surfaces with and without tungstate were 710.0 and 710.3 eV, respectively, and showed values closest to the 709.8 eV of  $Fe_3O_4$  among the reference materials. The small peaks shown at 706.0 eV correspond to metallic iron which originated from the substrates. The binding energy of W  $4f_{7/2}$  on the surface with tungstate was 35.2 eV, which was close to the binding energies of  $FeWO_4$  (35.3 eV) and  $WO_3$  (35.4 eV). The atomic ratio of W/Fe was roughly estimated to be 0.18 from a wide scan XPS spectrum by using atomic sensitivity factors. Although it was higher than 0.11 which was measured by STEM-EDS, they were in a possible range with consideration of difference in the measured areas and homogeneity of the film.

Based on these results, the characteristic features of the surfaces after dipping are summarized as follows.

- (1) With tungstate addition, an oxide and/or oxyhydroxide ultrathin film containing Fe and W was formed. The concentration of W in this film gradually increased and the crystallinity of the film decreased toward the top surface. The chemical state of Fe in the film was close to  $Fe_3O_4$ , and that of W was close to  $FeWO_4$  and  $WO_3$  among the reference materials. The atomic ratio W/Fe was 0.11 ~ 0.18.
- (2) Without tungstate addition, an iron oxide or oxyhydroxide ultrathin film, whose chemical state was close to  $Fe_3O_4$ , was formed. The crystallinity of the film was higher than that of the film with tungstate addition.

### C. Surface Structure after Corrosion Test

The surface after the corrosion test with tungstate addition was investigated in order to determine the role of the tungstate in the improvement in corrosion resistance. Figure 5 shows a plane view backscattered electron (BSE) image of the surface after the corrosion test with tungstate. The surface was categorized into three areas; the area where no film seemed to be formed (A), the areas covered with cracked films (B) and corrosion products (C). Most of the surface was classified into areas A or B.

Figure 6 shows cross-sectional TEM and SEM images of these areas. Cross-sectional TEM and SEM EDS spectra of the near-surface at these areas are shown in Fig. 7. The TEM-EDS spectra a and b, shown in Fig. 7(a), were measured at the circles indicated in Fig. 6(a) and (b), respectively. The SEM-EDS spectra c1-c4, shown in Fig. 7(b), were measured at the points indicated by cross marks in Fig. 6(c). The TEM observation and TEM-EDS measurements were carried out by Philips CM 20 FEG.

In area A, a ten nm thick film was observed in a high magnification TEM image, as shown in the inset in Fig. 6(a), although this film was not recognized by the plane view BSE image as shown in Fig. 5 or the lower magnification TEM image. This ultrathin film contained Fe, W, O and Na as shown in spectrum a in Fig. 7(a), although the measured area protruded from the thin film. From these results, it is supposed that the film observed in area A resembles that seen in Fig. 2.

In area B, a cracked film with several hundred nm thick was observed as shown in Fig. 6(b). And the steel sub-

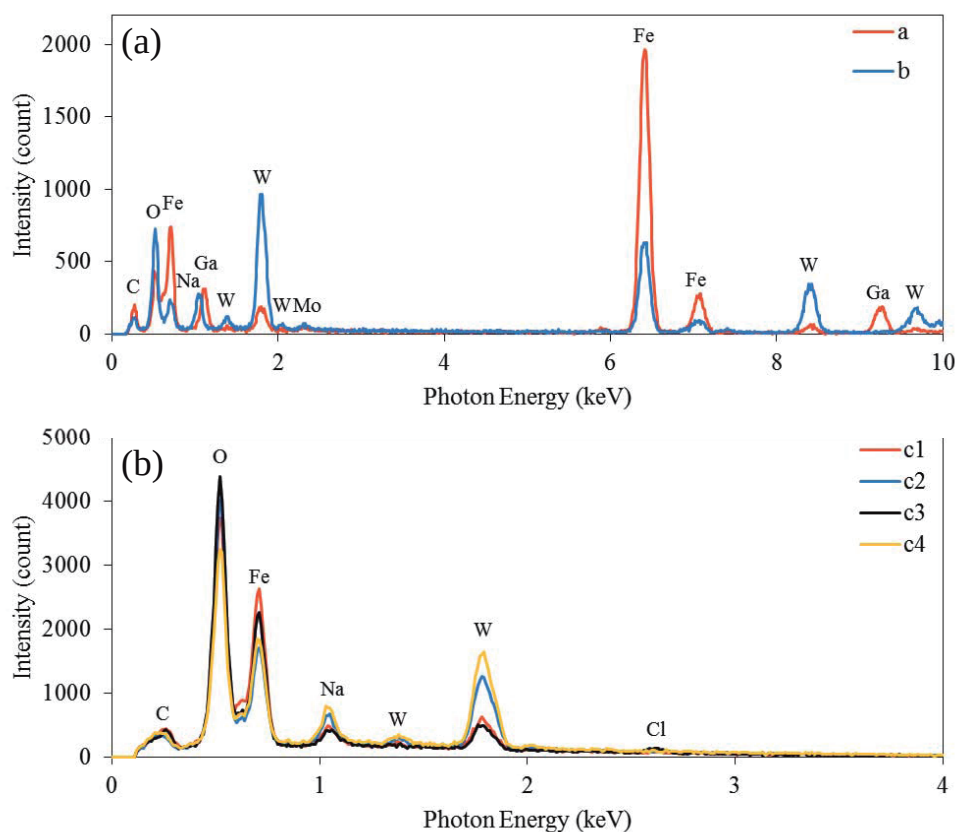


FIG. 7. TEM (a) and SEM (b) EDS spectra of the surface with tungstate addition after the corrosion test. Spectra a and b were measured at the circles indicated in cross-sectional TEM images Fig. 6(a) and (b), respectively. The TEM-EDS spectra were measured at  $E_P = 200$  keV. Ga and Mo peaks are due to FIB preparation and TEM grids, respectively. Spectra c1-c4 were measured at the cross marks indicated in Fig. 6(c). The SEM-EDS spectra were measured at  $E_P = 5$  keV.

strate under area B was protected from corrosion. The cracked film consisted of Fe, W, O and Na according to a TEM-EDS spectrum b in Fig. 7(a). These results suggest that the film seen in areas B also protected the surface from corrosion.

In area C, a corrosion pit was observed near the center, and the thickness of the corrosion products was on the order of several microns as shown in Fig. 6(c). Dense and porous rust layers were observed above and around the pit, respectively. In the dense layer, regions recognized as brighter and darker contrast in the BSE image (Fig. 6(c)) were observed. As both regions contained Fe, W, O and Na, the brighter region contained larger amount of W and Na as shown in the EDS spectra c1 and c2 in Fig. 7(b). As shown in the spectrum c3 in Fig. 7(b), the porous rust layer also contained those elements, and the intensities of Na and W were about the same level as the darker region in the dense layer. Moreover, small Cl  $K\alpha$  peak was detected only in the porous rust layer. Underneath of the porous rust layer, a cracked film was observed as indicated by arrows in Fig. 6(c). It contained larger amount of W and Na compared to other regions as shown in Fig. 7(b). This cracked film was considered to be identical to the film observed in area B shown in Fig. 6(b). Since the Cl peak was detected only in the porous rust layer, the dense rust layer and the cracked film were supposed to suppress diffusion of Cl toward the steel surface.

#### IV. DISCUSSION

An ultrathin film containing W was formed after dipping in the solution containing tungstate. It is suggested that this film remains even after the corrosion test, and improved corrosion resistance.

Tungstate is known as an inhibitor which forms a passivation film that suppresses the anodic process of iron corrosion, resulting in suppression of the nucleation and propagation of corrosion pits [7]. According to the potential-pH phase diagram for a Fe-W binary system [8],  $\text{FeOOH}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeWO}_4$  and  $\text{WO}_{2-3}$  can exist as stable phases under a near-neutral condition. From the diagram and the XPS results, it is assumed that  $\text{Fe}_3\text{O}_4$  is formed on the surface in the initial stage of dipping because pH increased due to elution of iron ions from the substrate. Subsequently, when  $\text{Fe}_3\text{O}_4$  has completely covered the surface, it is considered that  $\text{W}^{6+}$ , e.g.  $\text{WO}_4^{2-}$  and  $\text{WO}_3$ , is formed by neutralization of the solution near the interface between the solution and the surface, and as a result, the concentration of W in the upper layer increases. Since the atomic ratio W/Fe was  $0.11 \sim 0.18$ ,  $\text{W}^{6+}$  coexists in the  $\text{Fe}_3\text{O}_4$  film as a fine cluster or a substitution element. This may result in lowering of the crystallinity of the upper layer. The structure of the passivation film proposed in this study was in good agreement with the models by Sastri *et al.* [6] and Fujioka *et al.* [7]

The differences in the crystallinity of the film and the existence of  $W^{6+}$  with and without tungstate was clearly shown in this study. It is supposed that corrosion resistance is improved in the early stage by (1) suppression of diffusion of corrosion factors such as  $Cl^-$  by the low crystalline layer, (2) the barrier effect of  $W^{6+}$  in the film, which inhibits the corrosion reaction. Since grain boundaries in a crystalline film can provide a pathway for  $Cl^-$  toward steel substrate, a lower crystalline film which have smaller grain boundaries is supposed to prevent penetration of  $Cl^-$ . It is also supposed that existence of  $W^{6+}$  in a passive film results in suppression of  $Cl^-$  penetration by repulsion from  $WO_4^{2-}$  or formation of fine insoluble compounds such as  $FeWO_4$  [8].

It is considered that the steel surface was protected from corrosion during the test by this ultrathin film which was remained after the test (Fig. 6(a)). Since the film is not always formed homogeneously, some parts of the film could be destroyed by  $Cl^-$  and corrosion pits could form, as shown in Fig. 6(c). At the same time, it is supposed that iron ions eluted from the pits react with  $WO_4^{2-}$  in the solution to form thicker cracked films near the pits, as shown in Fig. 6(b). It is considered that these films also protect the surface from corrosion. Although corrosion reaction is progressed at pits,  $WO_4^{2-}$  segregates in the corrosion products above the pits, and it forms protective layer and prevents penetration of  $Cl^-$  resulting suppression of pit propagation [7, 8]. In fact, W segregated to brighter regions in the dense rust layer as shown in Fig. 6(c) and Fig. 7(b), diffusion of Cl was blocked by the dense rust layer. It is considered that addition of tungstate improved corrosion resistance on the whole surface during the corrosion test by this mechanism.

As the ultrathin film formed after dipping is mainly composed of  $Fe_3O_4$ , the film is still capable of including  $W^{6+}$  until it changes into  $FeWO_4$ . As the creation of  $W^{6+}$  can be controlled by the solution conditions, e.g., the

concentration of tungstate, pH and dissolved oxygen, it is supposed that the film properties can also be controlled by these conditions.

## V. CONCLUSION

The surfaces of steel specimens after dipping in a solution with or without tungstate, followed by a corrosion test, were investigated by various techniques in order to gain improved understanding of the role of tungstate in corrosion resistance. The corrosion reaction during the corrosion test was drastically suppressed when tungstate was added to the solution.

A crystalline film approximately 4 nm thick consisting of Fe and O was formed on the surface after dipping in the solution without tungstate. After dipping in the solution with tungstate, a film about 4 nm thick consisting of Fe, O and W was formed. This film consisted of two layers; the upper layer showed lower crystallinity and a higher W concentration. A film similar to this film remained even after the corrosion test, and that film improved corrosion resistance. It is supposed that (1) barrier properties are improved by the low crystalline layer or (2)  $W^{6+}$  in the film inhibits the corrosion reaction.

$WO_4^{2-}$  in the solution also protects the surface during the corrosion test. When the ultrathin film is destroyed,  $WO_4^{2-}$  reacts with iron ions eluted from corrosion pits to form thicker films near the pits, and pit propagation is also suppressed by segregation of  $W^{6+}$  in the corrosion products above the pits.

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