Growth Process of Passive Films on Austenitic Stainless Steels under Wet-dry Cyclic Condition

Rock-Hoon JUNG, Hiroaki TSUCHIYA and Shinji FUJIMOTO*

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 yamada-oka, Suita, Osaka, 565-0871 Japan. E-mail: fujimoto@mat.eng.osaka-u.ac.jp

(Received on February 1, 2012; accepted on March 15, 2012)

Passive films formed on Type 304 and 316 stainless steels under a wet-dry cyclic condition were characterized using X-ray photoelectron spectroscopy (XPS). Cr enrichment in the passive films during early stage of the wet-dry cycles occurred due to the preferential oxidation of Cr and the selective dissolution of Fe. However, the Cr fraction of hydroxide layer in passive film gradually decreased with time, because Fe(OH)₃ dissolved in the thin water layer were accumulated into the outermost hydroxide layer of a passive film during the dry condition. Chloride in thin water layer facilitated selective dissolution of Fe ions. On the other hand, the Mo in Type 316 stainless steel suppressed the dissolution of Fe ions. Consequently, Cr fraction in passive film on Type 316 became smaller than that of Type 304 stainless steel.

KEY WORDS: stainless steel; XPS; atmospheric corrosion; wet-dry cycle; passive films.

1. Introduction

Corrosion resistance of stainless steels depends on passive films, which consist of mainly Cr oxide and/or hydroxide. It is well known that the selective dissolution of Fe usually occurs on stainless steels in aqueous environment. This leads to the formation of Cr enriched passive films. As reported by many authors, Cr enrichment in passive film provides the high corrosion resistance of Fe–Cr alloy. However, even if the degree of Cr enrichment in the passive film is the same, corrosion resistance also depends on the structure and growth process of passive film. Therefore, the characterization of passive films is necessary for understanding high corrosion resistance of stainless steels.

Aqueous corrosion usually occurs in contact with a large volume of electrolyte. On the other hand, atmospheric corrosion occurs under thin water layer formed on the surface. When metals and alloys are exposed to a humid atmosphere, water molecular is adsorbed on the surface to form an extremely thin water layer. A thin water layer adsorbed on the surface strongly affects the properties of passive film on stainless steel. Cr enriched passive films, that are usually observed in aqueous solution, were hardly formed under atmospheric conditions. In the previous report, the authors demonstrated that Cr enrichment did not occur for passive films of Type 304 stainless steel in the atmosphere with relative humidities in the range of 30–70%, and that Cr content in passive films was comparable to the alloy composition. At relative humidity of 90%, however, slight Cr enrichment was recognized in passive films. It was concluded that a thin water layer kept remained on surfaces under such high relative humidity, so that Fe ions in passive films selectively dissolved into the thin water layer to form Fe(OH)₃. This resulted in the Cr enrichment of passive films under humid atmosphere. In our previous study, it is also reported that Cr enrichment in passive films under thin water layer containing chloride was facilitated significantly due to the accelerated dissolution of Fe. However, these results were obtained from experiments performed under constant relative humidity. Atmospheric corrosion tests exposed to the wet-dry cyclic condition have been required in order to reveal more realistic process of atmospheric corrosion. Some authors investigated corrosion mechanism on steels under wet-dry cyclic conditions using electrochemical techniques. Nishikata et al. and Cruz et al. monitored the corrosion rates of stainless steels and carbon steels with different nickel contents using an AC impedance method and a monitoring of corrosion potential under the cyclic wet-dry condition. Stratmann et al. also characterized atmospheric corrosion properties of pure iron under wet/dry transitions using Kelvin probe. Although numerous studies have been achieved on atmospheric corrosion under the wet-dry cyclic environment, the growth process and composition of passive films formed on stainless steel under the wet-dry cyclic condition have not been clarified yet. Therefore, in the present work, the authors examined changes in the composition and thickness of passive films formed on stainless steels under a wet-dry cyclic condition using X-ray Photoelectron Spectroscopy (XPS), and proposed a growth model of the passive films on stainless steels.

2. Experimental

Materials examined were Type 304 and 316 stainless steels. The chemical compositions of the materials are listed...
in Table 1. Specimen was dry-ground with #2000 SiC abrasive papers prior to corrosion tests. A wet-dry cyclic condition was achieved by the alternative exposure to a humid environment with the relative humidity of 90% and to a dry environment with the relative humidity of 5%. Each process was kept for one day. At the beginning of the wet cycle, a thin water layer was formed on the specimen surface by pouring distilled water for 10 s on the specimen which was rotated at 2 000 rpm using a spin coater. In order to examine the influence of chlorides on the chemical composition of passive film formed under the wet-dry cycle condition, a 0.1 M NaCl solution was used to form the thin water layer. The wet-dry cycle was repeated for desired periods. All experiments were carried out at 60°C. For comparison, a similarly prepared Type 304 stainless steel on which a thin water layer with chloride or without chloride was formed was kept in an air-tight container up to one week in which the relative humidity and temperature were controlled as 90% and 60°C, respectively. After the atmospheric corrosion tests, the specimen surface was rinsed with distilled water, and then dried in an air stream using a blower.

XPS analysis was carried out using a Rigaku XPS-7000 spectrometer. X-ray source employed was Al-Kα (250 W) without monochromator. The spectrometer was operated with constant pass energy of 15 eV. The take-off angle of photoelectron was perpendicular to specimen surface. The measured area on the specimen was approximately 6 mm in diameter. Typical XPS spectra obtained for Type 304 are shown in Fig. 1. Obtained spectra were separated into some chemical states using the deconvolution software attached to XPS-700 system. The Shirley method was used for background substration. The thickness and composition of passive films were quantitatively estimated from the integrated areas of the deconvoluted photoelectron spectra of the Fe2p3/2, Cr2p3/2, O1s, and C1s. The parameters for calculation used for the deconvolution are listed in Table 2. The intensity of Ni and Mo spectra were very weak. Therefore, Ni and Mo were not able to be incorporated in the quantitative analysis.

As generally recognized, passive films on stainless steels formed in aqueous environments consist of a Cr-enriched inner oxide layer and a covering hydroxide layer.18–20) Contaminant hydrocarbon is assumed to be on the hydroxide layer. Although composition of passive films under atmospheric environment may differ from that in aqueous solutions environments, structure of passive films will be essentially same in both environments. In the present work, therefore, thickness and composition of each layer in passive films were estimated with the similar process that are described in the authors’ previous publications.12,21)

3. Results

In the present work, thickness and composition of passive films formed under the wet-dry cyclic condition were characterized using XPS. As shown in Fig. 2(a), the thickness of passive film on stainless steels slightly increased in the early stage of cycles then became constant. On the other hand, when a thin water layer contains chloride (Fig. 2(b)), thickness of passive film remained constant from the early stage of cycles, and was quite similar to that formed without chloride. This indicates that chloride in a thin water layer does not necessarily affect the thickness of passive film.
under the wet-dry cyclic condition. Furthermore, it is found that the thickness of passive films on Type 304 and 316 stainless steels are almost same regardless of chloride in a thin water layer.

Figure 3 exhibits the ratio of $[\text{Cr}]/([\text{Cr}]+[\text{Fe}])$ in passive films exposed to the wet-dry cyclic condition. Cr fraction in the oxide layer of the passive film was larger than the Cr content in the substrate steel. Namely, slight Cr enrichment was recognized in the oxide layer formed under a thin water layer without chloride. The Cr content in the oxide layer on Type 304 stainless steel was similar to that on Type 316 stainless steel, although Cr content in the oxide layer of Type 316 was slightly smaller than in Type 304 stainless steel with chloride. In the hydroxide layer, the Cr content decreased with increasing the wet-dry cycles without chlorides (Fig. 3(a)). This indicates that Fe ions gradually transfer to the hydroxide layer during the wet-dry cycle. With chloride, on the other hand, the Cr content in hydroxide layer did not change with increasing wet-dry cycles. The Cr content in hydroxide layer of Type 304 stainless steel was slightly larger compared to the alloy composition, whereas Cr content in the hydroxide layer of Type 316 stainless steel is similar to the alloy composition. Therefore, chloride also affects compositions of passive films, especially in the hydroxide layer. It is noticeable that the wet-dry cycle does not affect thickness of passive films, but significantly changes their compositions.

In order to compare the passive films formed under the wet-dry cycle and the constant humidity conditions, specimens were subjected to a long-term exposure to a constant humidity condition with the relative humidity of 90% at 60°C. Figure 4 shows thickness of passive films formed on Type 304 stainless steel after exposure to the constant humid environment for various periods with and without chloride ion in the thin water layer. Chlorides have not changed the thickness of passive films. However, by comparing with the results described in Fig. 2, it is clearly recognized that passive films formed on Type 304 stainless steel under the constant humid condition were thinner than those formed under the wet-dry cyclic condition. These results indicate that the growth of passive films was facilitated during the dry environment.

4. Discussion

4.1. Change in the Chemical Composition of Passive Films during Wet-dry Cycles

In the present work, the constant thickness of passive films was observed under wet-dry cycles (the alternative exposure to the humid atmosphere with the relative humidity of 90% and the subsequent dry atmosphere with the humidity of 5% at 60°C), whereas chemical composition of
passive films drastically changed during the wet-dry cycles. Figs. 3(a) and 3(b) clearly show the Cr enrichment both in oxide layer and hydroxide layer in the early cycles without chloride. Some authors reported that Cr in stainless steels was preferentially oxidized under atmospheric condition. Therefore, Cr enrichment observed in the early stage of the wet-dry cycle can be attributed to the preferential oxidation of Cr.

In the constant humid condition without NaCl, the increase of the Fe content in the hydroxide layer proceeded as shown in Fig. 5(a). This may be due to the faster migration of Fe ions from the substrate steel than Cr ions. With increasing wet-dry cycle, the Fe content increased also in the hydroxide layer. Moreover, the Fe content in the hydroxide layer under prolonged wet-dry cycles further increased as shown in Fig. 3(a). According to Marcus et al., Fe ions in passive films could dissolve into the thin water layer to be Fe(OH)$_2$. These Fe(OH)$_2$ in the thin water layer could be adsorbed on a stainless steel surface during the dry condition and then accumulated into the hydroxide layer of a passive film. Therefore, the Fe content intensely increased in the hydroxide layer during the wet-dry cycles.

4.2. Effect of Chlorides on Chemical Composition of Passive Films Exposed to the Wet-dry Cycle

It has been reported that Cr enrichment of passive film in chloride ion containing aqueous solution is attributed to the selective dissolution of Fe into electrolyte to be Fe(Cl)$_3$. That is, the dissolution of Fe can be facilitated by chloride. Figure 6 shows the ratio of $[\text{Fe}^{2+}] / ([\text{Fe}^{2+}] + [\text{Fe}^{3+}])$ in the oxide layer of passive film formed on Type 304 and 316 stainless steels under the wet-dry cyclic condition. It is clear that the Fe(II) content in chloride-free thin water layer remained constant independent of the wet-dry cycle (Fig. 6(a)), whereas the Fe(II) content with chloride gradually decreased with the cycles (Fig. 6(b)). The diminution of Fe(II) could lead to the Cr enrichment in passive films formed on Type 304 stainless steel. Figure 7 presents the ratio of $[\text{Fe}^{2+}] / ([\text{Fe}^{2+}] + [\text{Fe}^{3+}])$ in the oxide layer of passive film formed on Type 304 stainless steel at 60°C under the constant humid environment. The relative humidity was kept at 90% during the experiment. As apparent, this result is similar to that obtained under the wet-dry cyclic environment, that is, the Fe(II) content in the presence of chloride decreased with time. This indicates that the dissolution of Fe(II) was facilitated by chloride during the wet-dry cycles.

In the case of constant humid condition, the selective dissolution of Fe into the thin water film results in Cr enrichment in both hydroxide and oxide layers of passive film as shown in Fig. 5. The accumulated Fe ions as salt could be removed when the specimen was rinsed with pure water before XPS analysis. On the other hand, for the wet-dry cycle condition with chloride as shown in Figs. 3(c) and 3(d), Cr contents both in hydroxide and oxide layers gradually increased in the early wet-dry cycles, then remained constant or decreased slightly. The initial increase of Cr for about 5 cycles, which is equivalent to 5 days, corresponds to the increasing Cr content in passive film observed in the constant humid condition. Further Cr enrichment could not proceed for subsequent wet-dry cycles. This might be because the periodic rinsing at the beginning of wet cycles hinders more accumulation of Fe ions in the thin water layer, or passive film changes during dry period more permeable for both Fe and Cr ions. The authors had predicted formation of much more Cr enriched passive films after wet-dry cycles with chloride. However, the dry condition in the present experiments was too low humidity and high temperature (relative humidity of approximately 5% and 60°C) which is not attainable in actual atmospheric condition. During such dry condition, passive film might be modified as “dry oxidation film” which is not protective in aqueous environment. Cr and Fe ions more easily migrate in such films than in the passive films formed in aqueous solution. If dry process were much mild, for instance 30–50% of relative humidity and room temperature, more Cr enriched passive film would be expected to form after exposure to more wet-dry cycles with chloride.

According to the results shown in Figs. 3(c) and 3(d), the selective dissolution of Fe ions hardly occurred on Type 316 stainless steel. According to the literature, Mo is an alloying element with a strong benefit to the pitting corrosion resistance of stainless steels. The alloyed Mo in austenitic stainless steels plays a role in forming the compact passive film. Newman et al. also inferred from the electrochemical transient experiments that Mo has made it difficult to dissolve the alloy components. Therefore, it is considered that Mo in Type 316 stainless steel suppressed the dissolution of Fe during the wet-dry cycles. This corresponds to that not only Cr enrichment is attributed to the corrosion resistance of stainless steel, the addition of Mo also improves the corrosion resistance of stainless steel in the environment containing chloride. In the present work, Cr enrichment in passive films formed on Type 304 stainless steels plays a role in forming the compact passive layer without and with 0.1 M NaCl solution at 60°C under relative humidity of 90%.
steel is higher than on Type 316 stainless steel (Figs. 3(c) and 3(d)). It was reported that the protectiveness of passive film was enhanced by Mo even when Fe content increased in the passive film.\textsuperscript{28} It means that Fe ions hardly dissolve into thin water layer because Mo leads to the formation of the more compact passive film. Therefore, the passive films on Type 316 stainless steel did not exhibit Cr enrichment under wet-dry cycle, but Type 316 stainless steel shows higher corrosion resistance than Type 304 stainless steel.

On the other hand, Ni also should affect the corrosion resistance of stainless steels. However, Ni is not clearly detected by XPS, because the concentration of Ni in the passive film on austenitic stainless steels are very low or below detection limits.\textsuperscript{29} Even if being not necessarily incorporated in the passive film, it is well known that Ni suppresses active dissolution, hinders reductive dissolution of passive films and en-nobles the pitting potential of austenitic stainless steels in chloride containing solutions.\textsuperscript{19,30,31}

4.3. Growth of Passive Films under Wet-dry Cyclic Condition

As mentioned above, the thin water layer on surface formed by humid atmosphere affects the composition of passive films on stainless steel. The change in the composition of passive films is accelerated by the constant humid condition, the wet-dry cycles and also chloride ions. Figure 8 presents schematically the growth process of passive film under humid atmospheres including the wet-dry cycles with and without chlorides based on the results and discussion described above.

In the early stage, for both the constant humid condition and wet-dry cycles, slight Cr enrichment occurs in passive films due to the preferential oxidation of Cr (Figs. 8(a)–8(d)). Fe ions in passive films may also selectively dissolve into the thin water layer to be Fe(OH)\textsubscript{aq} (Figs. 8(a) and 8(b)). Although the selective dissolution of Fe under constant humid condition caused Cr enrichment, the increase of the Fe content in the passive film gradually proceeded by the faster migration of Fe ions than Cr ions (Fig. 8(a)). In addition, the increase of Fe content in the hydroxide layer under wet-dry cycle is much accelerated than under constant humid condition. In the wet-dry cyclic condition, Fe(OH)\textsubscript{aq} dissolved in the thin water layer precipitates during dry period, and then presumably remain on the hydroxide layer. Therefore, the Fe content in the hydroxide layer increased during dry period by drying of the thin water layer containing dissolved Fe(OH)\textsubscript{aq} (Fig. 8(b)).

When the thin water layer contains chloride, Fe ions selectively dissolve of Fe into the thin water layer as Fe(Cl)\textsubscript{aq} (Figs. 8(c) and 8(d)). Therefore, Cr enrichment in passive film proceeds with time under constant humid condition (Fig. 8(c)) and also during wet periods of wet-dry cyclic condition (Fig. 8(d)).

5. Conclusions

In the present work, passive films of Type 304 and 316 stainless steels formed under the wet-dry cyclic condition were characterized using XPS, comparing passive films formed under constant humid condition. The following conclusions are drawn:

(1) In the early stage, Cr enrichment in the passive films of up to 30\% is attained due to the preferential oxidation of Cr.

(2) Fe ions in passive film selectively dissolve into the thin water layer to be Fe(OH)\textsubscript{aq}, which are accumulated into the outermost hydroxide layer of the passive films during the dry condition.

(3) Cr enrichment in the passive film is attributed to the selective dissolution of Fe into a thin water layer formed on surface and accelerated by chloride in the thin water layer.

(4) For the Type 316 stainless steel, Mo leads to the formation of the more compact passive film which suppresses Fe ions to dissolve into the thin water layer.

(5) Based on the experimental results, a growth model of passive films under humid atmospheric conditions including wet-dry cyclic condition is proposed.

Acknowledgements

The present work is supported by “Priority Assistance of the Formation of Worldwide Renowned Centers of Research – the Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design)” from the Ministry of Education, Sports, Culture Science and Technology of Japan.

REFERENCES