

# Synergistic Effect of Nitrogen and Molybdenum on Localized Corrosion of Stainless Steels

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(Received February 1, 2010; No Revision; Accepted February 25, 2010)

According to the bipolar model, ion selectivity of some species in the passive film is important factor to control the passivation. An increase of cation selectivity of outer layer of the passive film can stabilize the film and improves the corrosion resistance. Therefore, the formation and roles of ionic species in the passive film should be elucidated. In this work, two types of solution (hydrochloric or sulfuric acid) were used to test high N and Mo-bearing stainless steels. The objective of this work was to investigate the formation of oxyanions in the passive film and the roles of oxyanions in passivation of stainless steel. Nitrogen exists as atomic nitrogen, nitric oxide, nitro-oxyanions ( $\text{NO}_x^-$ ), and N-H species, not nitride in the passive film. Because of its high mobility, the enriched atomic nitrogen can act as a reservoir. The formation of N-H species buffers the film pH and facilitates the formation of oxyanions in the film.  $\text{NO}_x^-$  species improve the cation selectivity of the film, increasing the oxide content and film density.  $\text{NO}_x^-$  acts similar to a strong inhibitor both in the passive film and at active sites. This facilitates the formation of chromium oxide. Also,  $\text{NO}_x^-$  can make more molybdate and nitric oxide by reacting with Mo. The role of Mo addition on the passivation characteristics of stainless steel may differ with the test environment. Mo exists as metallic molybdenum, molybdenum oxide, and molybdate and the latter facilitates the oxide formation. When nitrogen and molybdenum coexist in stainless steel, corrosion resistance in chloride solutions is drastically increased. This synergistic effect of N and Mo in a chloride solution is mainly due to the formation of nitro-oxyanions and molybdate ion. Oxyanions can be formed by a 'solid state reaction' in the passive film, resulting in the formation of more molybdate and nitric oxide. These oxyanions improve the cation selectivity of the outer layer and form more oxide and increase the amount of chromium oxide and the ratio of  $\text{Cr}_2\text{O}_3/\text{Cr}(\text{OH})_3$  and make the film stable and dense.

**Keywords** : nitrogen, molybdenum, stainless steel, oxyanion, ion selectivity, bipolar model, synergistic effect

## 1. Introduction

In a chloride-containing environment, the effect of nitrogen additions for Mo-bearing stainless steels is more pronounced than for Mo-free stainless steels.<sup>1,2)</sup> To date, however, this effect has only been phenomenologically understood as a synergistic effect of N and Mo additions, and there is little understanding of the synergistic effect when N and Mo coexist in stainless steel. The pitting resistance equivalent (PRE) reveals the strong effect of nitrogen and molybdenum on pitting corrosion,<sup>3)</sup> and super stainless steels having a similar pitting resistance to Ti and Ni-base super alloys have been developed.<sup>4)</sup> In addition, an expression reflecting the synergistic effect between N and

Mo has recently been reported<sup>5)</sup>:  $\text{PRE} = \text{Cr} + 3.3 \text{ Mo} + 36 \text{ N} + 7 \text{ MoN} - 1.6 \text{ Mn}$ . Some suggestions on the synergistic effect between Mo and N can be summarized as follows: According to the work of Olefjord *et al.*,<sup>6)</sup> the synergistic effect between Mo and N is due to enrichment of Mo, Ni and Cr at the metal-electrolyte interface of initiated pits. The growth rate of the pits on the Mo-containing steel becomes lower than on the Mo-free alloy. Nitrogen is expected to compensate for the pH drop in the pits by reaction with  $\text{H}^+$  and formation of  $\text{NH}_3$  and  $\text{NH}_4^+$ . Repassivation is enhanced by the increased pH value in the pits and the higher concentration of Cr, which forms the passive film. Lu *et al.*<sup>7)</sup> explained this effect by the formation of nitrides on the surface of anodically polarized stainless steel, thus, inhibiting the transpassive dissolution of molybdenum. This effectively retains Mo

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in the passive surface, and thereby improves the localized corrosion resistance of stainless steel. Also, according to Olsson,<sup>8)</sup> the synergistic effect between nitrogen and molybdenum could result when nitrogen buffers the pH of the solution near the passive layer and, thus, alters the passive film environment to be more stable for compounds containing molybdates. Since the presence of molybdate in the passive film is an important parameter for the deprotonation rate in the film, molybdate would assist in the formation of ammonium. On the other hand, Kim *et al.*<sup>9),10)</sup> previously suggested that the synergistic effect comes from increased Mo enrichment and increased molybdate ion due to the cation selectivity of the NO<sub>3</sub><sup>-</sup> ion in the passive film. The increased cation selectivity could increase the ratio of Cr<sub>2</sub>O<sub>3</sub>/Cr(OH)<sub>3</sub>, the activation energy for pit initiation, and the repassivation rate.

Most of the above suggestions<sup>6),7),8)</sup> have focused on the increase of corrosion resistance and the reduction of passive current density by the addition of nitrogen and molybdenum to stainless steel. However, the addition of molybdenum increases the passive current density of stainless steels in sulfuric acid solutions.<sup>11)</sup>

According to the bipolar model,<sup>9),10),11),12),13),14),15)</sup> ion selectivity of some species in the passive film is important factor to control the passivation. An increase of cation selectivity of outer layer of the passive film can stabilize the film and improves the corrosion resistance. Of course, inverse case is possible. Therefore, the formation and roles of ionic species in the passive film should be elucidated. In this work, two types of solution (hydrochloric or sulfuric acid) were used to test high N and Mo-bearing stainless steels. The objectives of this work were to investigate the formation of oxyanions in the passive film and the roles of oxyanions in passivation of stainless steel.

## 2. Experimental methods

The stainless steels evaluated in this study were prepared from high purity grades of Fe, Cr, Ni, Mo, Fe-Cr-N, Fe-Si, and Fe-Mn. After melting in a high frequency vacuum induction furnace, only solid sections of the cast ingots

were taken to prepare the specimens. The sections were first soaked 120 minutes and hot rolled to 6 mm at 1,250 °C. The hot rolled specimens were annealed at 1125 °C for 10 minutes, water quenched, and acid pickled. A small section was cut after each procedure and was used for chemical analysis. Table 1 presents the chemical compositions of the experimental alloys.

The experimental alloys were cut into 2 x 2 cm and ground to SiC paper - #600 grit. The critical pitting temperature (CPT) was determined according to ASTM G48, by immersion in 6% FeCl<sub>3</sub> and "green death" solution (7% H<sub>2</sub>SO<sub>4</sub> + 3% HCl + 1% CuCl<sub>2</sub> + 1% FeCl<sub>3</sub>) for 24 hours at each temperature tested. In this work, CPT indicates the temperature where the accumulated weight loss for each test temperature exceeds 5 mg. After immersion the specimen surface was examined by optical microscope to detect pitting.

Anodic polarization tests were performed in hydrochloric or sulfuric acid solution using an EG&G Par Model 273A potentiostat. All specimens were ground to SiC paper - #600 grit. The solutions were deaerated by purging with prepurified nitrogen gas (90 ml/min) for 30 minutes before specimen immersion. After immersion, the sample was cathodically polarized for 10 minutes at -700 mV (SCE). Specimens were potentiostatically held for 10 minutes at open circuit potential and subsequently polarized anodically from the corrosion potential at a scan rate of 1 mV/sec. A saturated calomel electrode (SCE) was utilized as the reference and high-density graphite rods were used as counter electrodes.

Electrochemical impedance spectra were generated at passive state (+600 mV(SCE)) over a frequency range between 600 KHz and 5 mHz using a Schlumberger Solatron 1250 Frequency Response Analyzer(FRA) in combination with a Solatron 1286 potentiostat.

X-ray Photoelectron Spectroscopy (XPS) was conducted to analyze the surface species of the passive film of the specimen. In order to form a passive film on the specimen, an anodic potential, +600 mV (SCE), was applied to the specimen for 1 hours in a 6 N H<sub>2</sub>SO<sub>4</sub> solution. All XPS measurements were carried out in a Model 5700 ESCA

**Table 1. Chemical compositions of the experimental alloys**

(wt.%)

No.	Cr	Mo	N	Ni	Mn	C	Si	S	P	Fe	PRE1	PRE2
A1	22.9	0.01	0.36	13.0	0.50	0.02	0.42	0.005	0.003	Bal.	33.7	35.1
A2	23.1	1.04	0.39	14.1	0.47	0.02	0.44	0.004	0.004	Bal.	38.2	42.7
A3	23.1	4.52	0.43	17.5	0.47	0.03	0.44	0.003	0.009	Bal.	50.9	66.8
A4	23.2	5.66	0.44	18.5	0.46	0.02	0.45	0.003	0.011	Bal.	55.1	74.4

\* PRE1 = Cr + 3.3Mo + 30N, PRE2 = Cr + 3.3Mo + 36N + 7MoN - 1.6Mn

system (Perkin-Elmer Co.) using an Al-K $\alpha$  excitation (1486.6 eV). Take-off angles were 15, 45, 75°. All XPS-spectra were corrected for the charge shift taking the carbon spectrum from adventitious carbon at 284.6eV. A satellite subtraction program, depending on the analyzer pass energy, was employed to eliminate the X-ray satellite. A Lorentian/Gaussian convolution program was used for peak synthesis. To minimize the effect of air-formed oxide during the transfer to XPS instrument, every sample was sputtered for 0.3 min. The noise level for nitrogen was suppressed by utilizing very long acquisition times (20 min.) for each nitrogen spectrum.<sup>8)</sup>

### 3. Results

Fig. 1 shows the effect of Mo and N additions on the critical pitting temperature in 6% FeCl<sub>3</sub> and "green death" solutions. Increasing the PRE value (i.e. increasing Mo) improves corrosion resistance in chloride solution. Alloy A3 that contain high Mo and high N content exhibited a CPT above the boiling point of the test solution. That is, PRE2 value (Cr + 3.3Mo + 36N + 7MoN - 1.6Mn) of A3 is 66.8. The PRE2 equation<sup>5)</sup> incorporates the synergistic effect of N and Mo additions. The low Mo alloy, A2, exhibits a CPT of 50-60 °C; however, other alloys (Fe-28Cr-3Ni-4Mo) with a similar PRE value (ca. 42) exhibit a much higher CPT of 90 °C.<sup>14)</sup> This suggests that the synergistic effect on pitting corrosion can be effective in high Mo and N stainless steel.

Fig. 2a reveals the effect of Mo and N additions on the anodic polarization behavior at a scan rate of 1 mV/sec in 50 °C, 1.5 N HCl solution. The low Mo alloy, A2 exhibited high passive current density. With increasing Mo additions (A3), there is a slight increase in the corrosion potential in conjunction with a decrease in both critical current density and passive current density. Also, increasing Mo and N contents, AC impedance in the passive film was increased as shown in Fig. 2b.

Fig. 3a shows the effect of Mo and N additions on the anodic polarization behavior at a scan rate of 1 mV/sec in 50 °C, 6N H<sub>2</sub>SO<sub>4</sub> solution. In general, the corrosion potential increased and the critical current density decreased as a function of increasing Mo content. Conversely, in contrast to the behavior in HCl, the passive current density increased with the addition of Mo. It has previously been reported<sup>10),11)</sup> that, even in the event of similar corrosion potentials, the addition of Mo increased passive current density in sulfuric acid. To date explanations within the literature to account for the effect of Mo on passivation are incomplete as they have been unable to account for this phenomenon.<sup>13),16),17)</sup> One aim of this work is, there-

fore, to provide a general understanding of passivation behavior as a function of Mo and N additions. Also, increasing Mo and N contents, AC impedance in the passive film was reduced as shown in Fig. 3b.

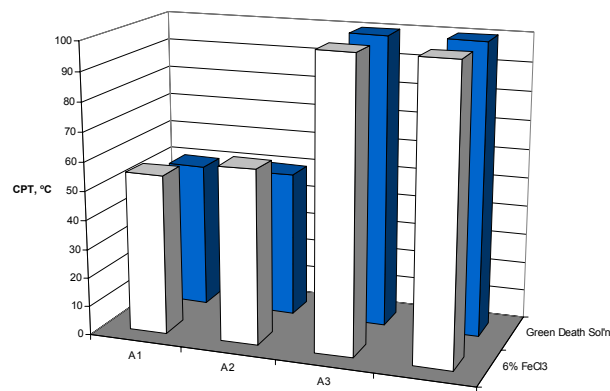


Fig. 1. Critical pitting temperature in 6% FeCl<sub>3</sub> and 'green death' solution.

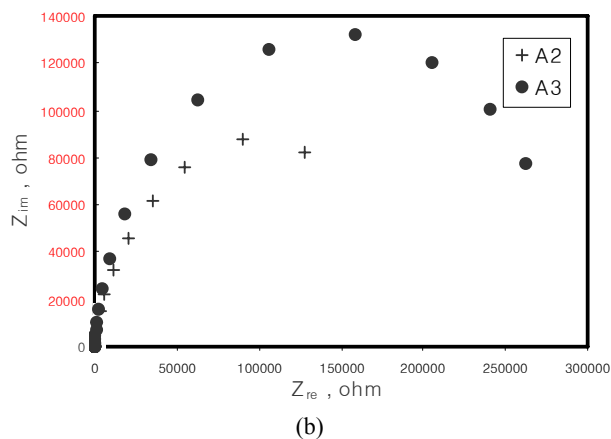
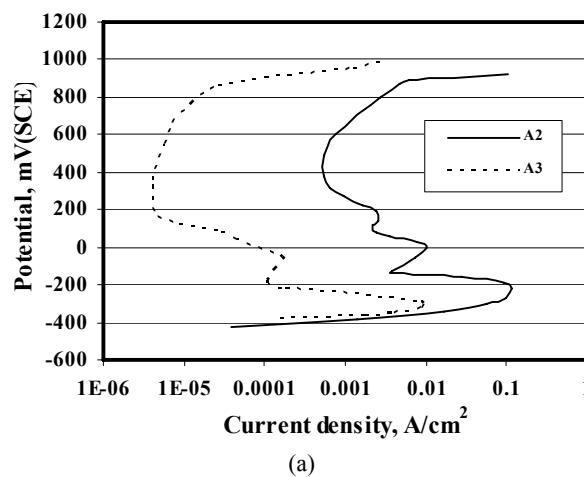


Fig. 2. Effects of Mo and N on the polarization behavior and the impedance of passive films; (a) 50 °C 1.5 N HCl, 1 mV/sec, (b) 1 hr passivated at +400 mV(SCE).

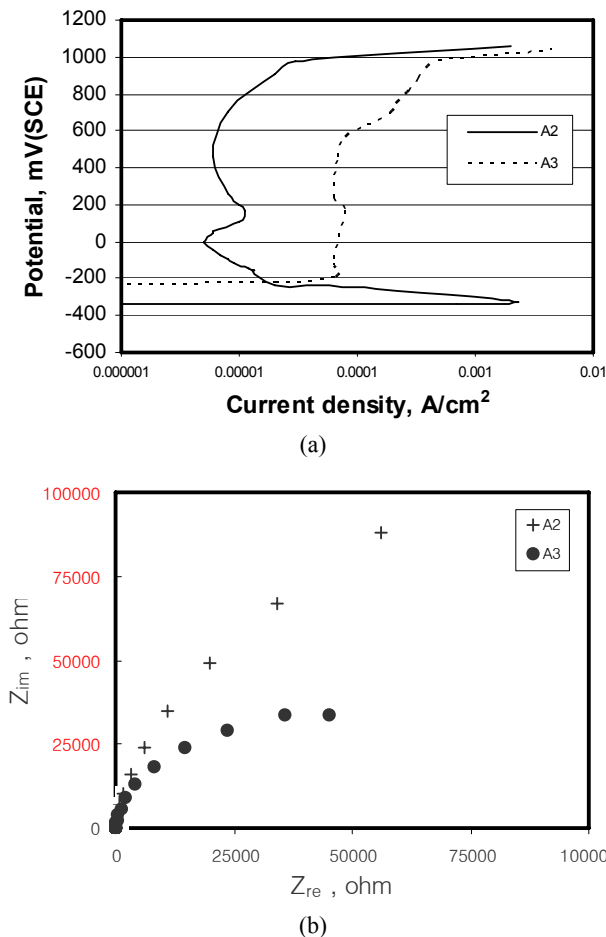


Fig. 3. Effects of Mo and N on the polarization behavior and the impedance of passive films; (a) 50 °C 6 N H<sub>2</sub>SO<sub>4</sub>, 1 mV/sec, (b) 1 hr passivated at +400 mV(SCE).

Figs. 4 (a - c) present XPS spectra for N<sub>1s</sub> from the passive film formed on alloy A1 (Mo-free) and Figs. 5 (a - c) present corresponding spectra for alloy A4 (Mo-bearing). In both cases the passive film was formed in a 6 N H<sub>2</sub>SO<sub>4</sub> solution (50 °C) at an applied potential of +600 mV (SCE). (Take-off angle: a-15°, b-45°, c-75°). As presented in these figs., for the Mo-free stainless steel (A1), nitrogen exists as atomic nitrogen, N-H species (NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>), nitric oxide (NO), and nitro-oxyanions (NO<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>). In the Mo-bearing stainless steel, because the N<sub>1s</sub> peak overlaps the Mo<sub>3p</sub> peak, the Mo<sub>3p</sub> peak should be considered. As in the case of the Mo-free alloy, nitrogen exists as atomic nitrogen, N-H species, nitric oxide, and nitro-oxyanions. Detection of nitric oxide and nitro-oxyanions is contrary to earlier findings<sup>7),18),19),20)</sup> and it will help to provide a more general explanation of passivation behavior. Fig. 5 reveals the effect of Mo on the atomic nitrogen, nitro-oxyanions and N-H species content. An increase in Mo, resulted in an increase in atomic nitrogen

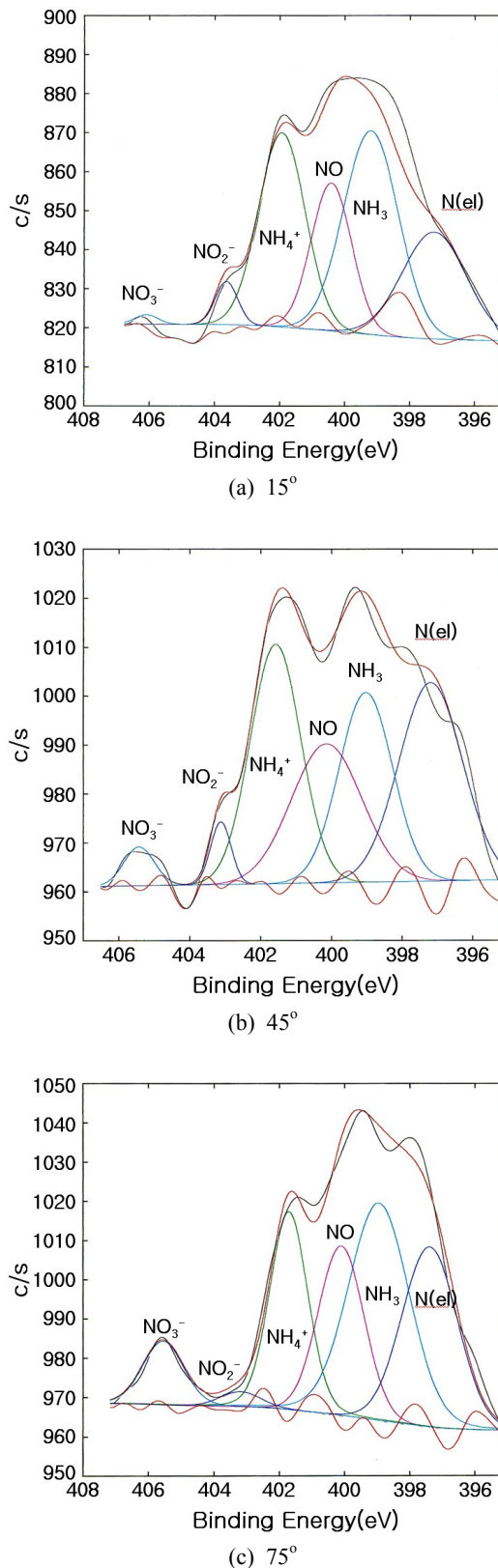
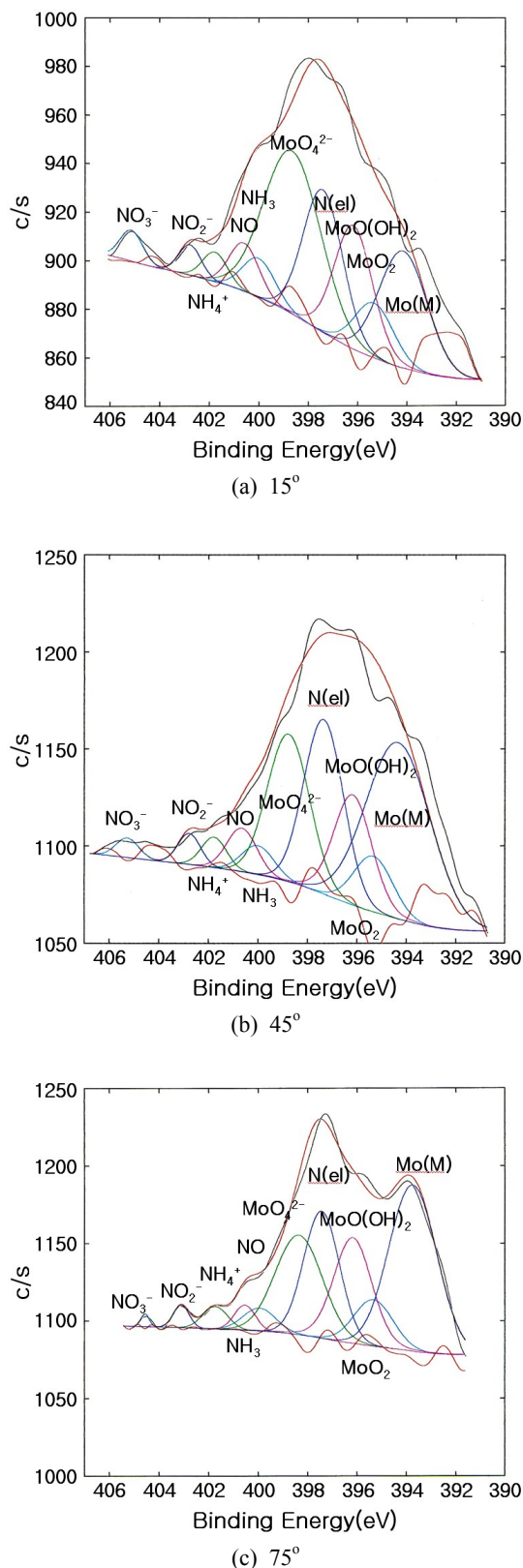


Fig. 4. Chemical states of nitrogen by XPS in the passive film of Alloy A1 formed in a 6 N H<sub>2</sub>SO<sub>4</sub> solution (50 °C) at an applied potential of +600 mV (SCE). (Take-off angle: a-15°, b-45°, c-75°).



**Fig. 5.** Chemical states of nitrogen by XPS in the passive film of Alloy A4 formed in a 6 N H<sub>2</sub>SO<sub>4</sub> solution (50 °C) at an applied potential of +600 mV (SCE). (Take-off angle: a-15°, b-45°, c-75°).

and nitro-oxyanions; however, it also resulted in a decrease in N-H species. Clayton *et al.*,<sup>13,21)</sup> previously suggested that, for Mo bearing alloys the higher Cr<sub>2</sub>O<sub>3</sub>/Cr(OH)<sub>3</sub> ratio formed in HCl solutions is due in part to the role played by MoO<sub>4</sub><sup>=</sup> in the outer region of the passive film and MoO<sub>4</sub><sup>=</sup> anion may convert the anion selective hydrated oxides to cation selective phases. Therefore, the decreased ratio of Cr<sub>2</sub>O<sub>3</sub>/Cr(OH)<sub>3</sub> reveals that MoO<sub>4</sub><sup>=</sup> formation by Mo addition may alter the ion selectivity of the passive film from cation selective to anion selective.<sup>15)</sup>

## 4. Discussion

### 4.1 Formation of nitro-oxyanions and nitric oxide

Since Osozawa *et al.*<sup>22)</sup> reported the formation of ammonium in the solution during corrosion testing of N bearing steels, as summarized as Table 2, many researchers have studied the formation of soluble species. As tabulated below, many papers report the formation of soluble nitrogen species. Most papers, except that of Kim *et al.*,<sup>9)</sup> considered that NH<sub>4</sub><sup>+</sup> ion may be formed through reaction and NO<sub>3</sub><sup>-</sup> ion may be formed through the reaction of NH<sub>4</sub><sup>+</sup> + 3H<sub>2</sub>O → NO<sub>3</sub><sup>-</sup> + 10H<sup>+</sup>. Kim *et al.* tested Fe - 20Cr - 4Ni - 6.5Mo - 0.28N stainless steel in aqueous 1.5N HCl. They report finding nitrate and ammonium ions in the electrolyte by ion chromatography and that the formation of nitro-oxyanion may be possible through the solid state reaction: N + 6OH<sup>-</sup> → NO<sub>3</sub><sup>-</sup> + 3H<sub>2</sub>O + 5e<sup>-</sup> (typical reaction) in the passive film. Kim<sup>23)</sup> also studied the effect of nitrate, nitrite, and ammonium ions on the passivation of stainless steels. The results indicate a decrease in passive current density for nitrate and nitrite ions; however, ammonium ion increases the passive current density. For the structure of the passive film, in the case of N-bearing stainless steel, nitrogen exists as atomic nitrogen, nitric oxide, and nitro-oxyanion; however, for N-free stainless steel in a nitrate containing solution, atomic nitrogen was not detected at any depth and the majority of the film consisted of nitrate and nitrite.

However, recently, D. Kim *et al.*<sup>24)</sup> reported the formation of nitrate is not possible. They polarized N-free stainless steels cathodically in 0.1 M HCl + 0.5 M NaNO<sub>3</sub> and then performed an anodic polarization test and XPS measurement. They concluded that there was no evidence to suggest that the N constituent of N-containing stainless steels anodically oxidized to nitrate, and the role of the surface nitride formed cathodically from NO<sub>3</sub><sup>-</sup> ions is analogous to that formed from anodic segregation of nitrogen in N alloyed steel. Olsson<sup>8)</sup> noticed that there is a possibility for the formation of soluble oxidized species via the reaction NH<sub>4</sub><sup>+</sup> + 2H<sub>2</sub>O → HNO<sub>2</sub> + 7H<sup>+</sup> + 6e<sup>-</sup>, however,

**Table 2. Result of solution analysis of N-bearing stainless steels**

Authors (year)	Alloys	Test solutions	Detected Species in solution	References
Osozawa <i>et al.</i> (1975)	23Cr-22Ni-1.5Mo-N	20%FeCl <sub>3</sub> 6H <sub>2</sub> O	NH <sub>4</sub> <sup>+</sup>	22
Kim <i>et al.</i> (1989)	20Cr-4Ni-6.5Mo-0.28N	1.5N HCl (anolyte & passive film)	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	9
Hanju <i>et al.</i> (1991)	20Cr-12Ni-2Mo-N	1% HCl (anolyte)	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	26
Komori <i>et al.</i> (1992)	316LN	3.5% NaCl (anolyte)	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	26
Tsai <i>et al.</i> (1993)	18Cr-19Mn-N	1% NaCl (SSRT)	NH <sub>4</sub> <sup>+</sup>	26
Shirage <i>et al.</i> (1993)	316LN	3.5% NaCl (anolyte)	NO <sub>3</sub> <sup>-</sup>	26
Palit <i>et al.</i> (1993)	316LN	1N HCl	NH <sub>4</sub> <sup>+</sup>	26
Komori <i>et al.</i> (1995)	316LN	1000ppm Cl <sup>-</sup> (anolyte)	NO <sub>3</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	26

he concluded it may be dispersed in the solution and not observed during surface analysis. Moreover, Vanini *et al.*<sup>25)</sup> reported that N-H or N-O peaks may come not only from the bulk nitrogen but also from nitrogen-containing species present at trace level in the solution. On the other hand, Kim *et al.*<sup>9)</sup> reported that by using ion spectroscopy, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions were detected in anolytes formed at passivation potentials (+400 mV (SCE)) of Mo and N bearing stainless steel, but not for Mo-free stainless steel (0.21% N).

Fe is easily dissolved in both the active and passive state and, therefore, other elements can be relatively enriched. In the passive state, Fe was still dissolving even though iron oxide formed; however, Cr, Mo and N all formed stable oxides. A higher Cr enrichment was observed for films formed in the passive region than in the active region; however, the opposite was true for both Mo and N, which exhibited a lower enrichment in the case of active dissolution. This suggests that Mo and N enrichment during active dissolution may produce soluble species (as like MoO<sub>4</sub><sup>=</sup> and NO<sub>3</sub><sup>-</sup>) in the passive film during passivation. These oxy-anions can partially dissolve and have been detected in anolytes;<sup>9),10),11)</sup> thus, less Mo and N are detected in the passive film than in the active region. On the other hand, if the enriched Mo, N, and Cr observed during active dissolution had formed mixed nitrides, the extent of enrichment in the passive region should have remained approximately constant since nitrides are chemically and electrochemically very stable.

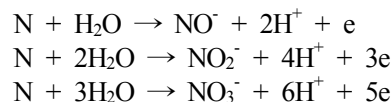
As presented in Fig. 5, nitro-oxyanions (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO) and nitric oxide (NO) were detected. How could nitro-oxyanions and nitric oxide be formed?

During active dissolution, N can form NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> via a cathodic reaction as in reaction and  $N + 3H^+ + 3e \rightarrow NH_3$ . So, N reduces the active dissolution rate of the steel and is enriched during dissolution. In addition, for acidic conditions Fe is very soluble in both the active and

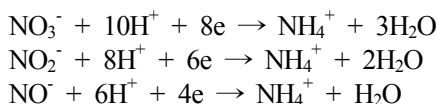
passive region and dissolves easily. This selective dissolution behavior facilitates the enrichment of other elements during active dissolution or in the passive state (It should be noted, however, that in alkaline solution, Fe oxidized and was not depleted in the passive state). Therefore, nitrogen suppresses active dissolution and buffers the pH of the passive film due to the formation of NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>.

During dissolution and passivation, enriched nitrogen acts as a reservoir for several inhibiting reactions because of its high mobility, as shown by the work of Olsson.<sup>8)</sup> He showed nitrogen enrichment at the metal/oxide interface above both the ferrite and austenite phase of duplex stainless steel. As nitrogen solubility in ferrite is very small, the high level of nitrogen in the passive film above the ferrite indicates high mobility. Thus, it is considered that when depassivation occurs, the enriched nitrogen can migrate and form inhibiting species (for examples, NO<sub>3</sub><sup>-</sup>, NO, NH<sub>4</sub><sup>+</sup> etc.).

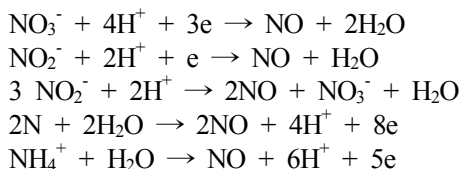
Because excess OH<sup>-</sup> and NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> are formed in the passive film, local passive film pH would be high. Thus, nitro-oxyanions such as NO<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> can be formed by a 'solid state reaction'<sup>13),27)</sup> in the passive film even at low electrode potentials. Typical reactions that may be considered are as follows:



Oxyanions formed in the passive film may be soluble in part, and some ions have been detected in the anolyte.<sup>9),11)</sup> Also, these oxyanions may be reduced and then ammonium ion can be easily detected both in the film<sup>7),18),19),20),24)</sup> and in the solution.<sup>26)</sup> Typical reactions, which may be considered, are as follows;



Also, nitric oxide can be formed from these nitro-oxyanions or atomic nitrogen and other species as in the following reactions;



Moreover, molybdenum and tungsten can be oxidized to molybdate and tungstate and can make nitric oxide in nitrate-nitrite as follows;<sup>28)</sup>



The simplest representative of nitrogen oxides is nitric oxide (NO). Nitric oxide readily reacts with free radicals and acts as an effective inhibitor. In the form of a neutral molecule, nitric oxide can combine with salts of many metals to form stable complexes - for example, nitroxyl iron sulfate -  $\text{Fe}(\text{NO})\text{SO}_4$ ,<sup>29)</sup> or nitroxyl molybdenum chloride -  $\text{MoCl}_2(\text{NO})_2$ .<sup>30)</sup>

For nitric oxide formation, many papers<sup>31),32),33),34),35)</sup> confirm that adsorbed nitric oxide is the species formed from nitrite solutions and these adlayers are stable over a wide range of electrode potentials.<sup>33)</sup> Both nitroxyl compounds<sup>36)</sup> and nitric oxide adlayers formed.<sup>31)</sup>

Ibbotson *et al.*<sup>37)</sup> studied the chemisorption of NO on Ir using X-ray and UV-photoelectron spectroscopy, Auger electron spectroscopy, LEED etc. They believe the atomic recombination reaction on the surface is important. They report that XPS of NO yields the  $\text{O}_{1s}$  and  $\text{N}_{1s}$  levels of NO at 531.5 and 400.2 eV, respectively, with or without oxygen present and the oxygen overlayers tend to stabilize NO. Another XPS result by Sugai *et al.*<sup>38),39)</sup> indicates that the binding energies of atomic nitrogen and NO are 397.0 and 400.4 eV respectively. Breitschaffer *et al.*<sup>40)</sup> reported that NO can be formed on Ni at room temperature and the binding energies of  $\text{N}_{1s}$  and  $\text{O}_{1s}$  levels of NO are  $400.0 \pm 0.2$  and  $530.7 \pm 0.2$  eV respectively.

Agrawal *et al.*<sup>41)</sup> indicate that all surfaces contain defects. These can be defined as sites with a lower degree of coordination than the maximum possible for a particular crystallographic face. Defects on well-ordered low index single crystal surfaces are mainly in the form of step and kink sites and are present in small concentrations. In con-

trast, low coordination edge and corner atoms can be in the majority on small metal particles of supported metal crystals. Because molecules chemisorb more strongly on the defect atoms, such atoms can have a disproportionately large influence on surface chemical reactions. They reported that NO adsorbs molecularly both at terrace and defect sites.

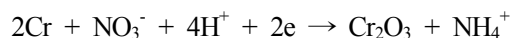
#### 4.2 Effect of N and Mo on pit propagation

If any pits were formed, local chemistry might be changed to low pH and high aggressive ions, and high electric field might be formed in pitted area. Moreover, many active sites such as kink and terrace etc. could be formed in pitted face. High electric field will do active dissolution of pitted area and then N and Mo could be segregated at pitted area. Also, nitrogen may move into active sites easily because of high mobility of N.

Segregation of N and Mo facilitates the repassivation of pitted area; segregated nitrogen makes ammonium ion and nitro-oxyanions and nitric oxide. Ammonium ion can increase the local pH, and nitro-oxyanions and nitric oxide strengthen the oxide and facilitate the formation of chromium oxide, and atomic nitrogen moves to kink and step sites and then reduces the dissolution of active sites. Partly dissolved molybdate and  $\text{NO}_x^-$  ions act as corrosion inhibitors in pitted area, and molybdate and  $\text{NO}_x^-$  ions in repassivated film increase the cation selectivity of the film and then facilitate the formation of chromium oxide. As described above, stainless steel having N and Mo additions is strong to localized corrosion and the repassivation rate can be increased with high N and Mo additions.

#### 4.3 Synergistic effect of N and Mo additions in chloride solution

The role of nitrogen on corrosion and passivation of stainless steel can be summarized as follows; Nitrogen exists as atomic nitrogen, nitric oxide, nitro-oxyanion ( $\text{NO}_x^-$ ), or N-H species in the passive film. The enriched atomic nitrogen acts as a reservoir because its mobility is high. The formation of N-H species buffers the pH of the film and facilitates the formation of oxyanions in the film.  $\text{NO}_x^-$  species improve the cation selectivity of the film.<sup>9),23)</sup> It makes the film more oxide and dense.  $\text{NO}_x^-$  acts as a strong inhibitor in both film and active sites and facilitates the formation of chromium oxide: for example,



Thus, N-H species can easily be detected but  $\text{NO}_x^-$  species can hardly be detected in the film. Also,  $\text{NO}_x^-$  can make more molybdate (or tungstate) and nitric oxide with Mo

(or W) by the above reaction. Thus, the synergistic effect of N and Mo is revealed.<sup>4),5),42)</sup>

However, the role of the addition of Mo on the passivation of stainless steel is different in different environments, for example in hydrochloric or sulfuric acid solutions. As shown in Figs. 1 and 2, Mo improves the corrosion resistance and reduces the passive current density of stainless steel in chloride solutions; however, in sulfuric acid, Mo increased the passive current density as presented in Fig. 3. To date, previous suggestions have been unable to account for the observed passive current density increase as a result of the addition of Mo.<sup>11),14)</sup> One potential key point for that mechanism is a variation in the ion selectivity of molybdate as a function of the environment; however, this is beyond the scope of this paper, which focuses on the effect of Mo in chloride solution. As others have described,<sup>11),13),21)</sup> Mo exists as metallic molybdenum, molybdenum oxide, or molybdate. Molybdate facilitates the formation of oxides on the basis of the bipolar model.

Where does 'synergistic effect' of Mo and N additions come from? In the passive film, nitro-oxyanions and molybdate ion can be formed thermodynamically. Favorable thermodynamic conditions for the formation of these ions, which are unstable in acid solutions, could be provided by the presence of excess OH<sup>-</sup> and NH<sub>4</sub><sup>+</sup> ion. These oxyanions can be formed via a 'solid state reaction' in the passive film, and more molybdate and nitric oxide can be formed through the following reaction ( $\text{Mo} + 4\text{NO}_2^- \rightarrow \text{MoO}_4^{2-} + 4\text{NO} + 2\text{e}^-$ ) in N and Mo bearing stainless steel. More oxyanions will increase the property of cation selectivity and more oxide will be formed and, thus, the synergistic effect of N and Mo additions may develop. That is, in chloride solutions, more oxyanions improve the cation selectivity of the outer layer, form more oxide and increase the amount of chromium oxide and the ratio of Cr<sub>2</sub>O<sub>3</sub>/Cr(OH)<sub>3</sub> and make the film stable and dense. Even in low pH solution, the effect of nitrogen becomes stronger than N-free alloys and this is due to buffering of the local pH by NH<sub>4</sub><sup>+</sup> ion formation.

## 5. Conclusions

1) Nitrogen exists as atomic nitrogen, nitric oxide, nitro-oxyanions (NO<sub>x</sub><sup>-</sup>), and N-H species, not nitride in the passive film. Because of its high mobility, the enriched atomic nitrogen can act as a reservoir. The formation of N-H species buffers the film pH and facilitates the formation of oxyanions in the film. NO<sub>x</sub><sup>-</sup> species improve the cation selectivity of the film, increasing the oxide content and film density. NO<sub>x</sub><sup>-</sup> acts similar to a strong inhibitor both in the passive film and at active sites. This facilitates

the formation of chromium oxide. Also, NO<sub>x</sub><sup>-</sup> can make more molybdate and nitric oxide by reacting with Mo. The role of Mo addition on the passivation characteristics of stainless steel may differ with the test environment. Mo exists as metallic molybdenum, molybdenum oxide, and molybdate and the latter facilitates the oxide formation.

2) When nitrogen and molybdenum coexist in stainless steel, corrosion resistance in chloride solutions is drastically increased. This synergistic effect of N and Mo in chloride solutions is mainly due to the formation of nitro-oxyanions and molybdate ion. Oxyanions can be formed by a 'solid state reaction' in the passive film, resulting in the formation of more molybdate and nitric oxide. These oxyanions improve the cation selectivity of the outer layer and form more oxide and increase the amount of chromium oxide and the ratio of Cr<sub>2</sub>O<sub>3</sub>/Cr(OH)<sub>3</sub> and make the film stable and dense.

## References

1. A. Hoshino, *J. of ISIJ*, **16**, 2279 (1986).
2. Y. S. Park and S. T. Kim, *J. Corrosion Sci. Soc. of Korea*, **12**, 1 (1983).
3. J. O. Nilsson, *Materials Sci. and Tech.*, **8**, 685 (1992).
4. Y. S. Park and Y. S. Kim, 13th International Corrosion Congress, Australia, paper No.384, Nov. 30 (1996).
5. R.F.A.Jargelius-Pettersson, *Corrosion*, **54**, 162 (1998).
6. I. Olefjord and L. Wegrelius, *Corrosion Science*, **38**, 1203 (1996).
7. Y. C. Lu, M. B. Ives, and C. R. Clayton, *Corrosion Science*, **35**, 89 (1993).
8. C. O. A. Olsson, *Corrosion Science*, **37**, 467 (1995).
9. Y. S. Kim and Y. S. Park, *J. Corrosion Sci. Soc. of Korea*, **18**, 97 (1989).
10. Y. S. Kim and Y. S. Park, *J. Corrosion Sci. Soc. of Korea*, **18**, 89 (1989).
11. Y. S. Kim, *Metals and Materials*, **4**, 183 (1998).
12. G. P. Halada, D. Kim, and C. R. Clayton, *Corrosion*, **52**, 36 (1996).
13. C. R. Clayton and Y. C. Lu, *J. Electrochem. Soc.*, **133**, 2465 (1986).
14. Y. S. Kim and J. Kim, *J. Corrosion Sci. Soc. of Korea*, **26**, 435 (1997).
15. M. Sakashita and N. Sato, Passivity of Metals, R. P. Frankenthal and J. Kruger, eds., p. 479, The Electrochemical Society, Princeton, NJ (1978).
16. C. Leygraf, G. Hultquist, I. Olefjord, B. O. Elfstrom, V. M. Knyazheva, A. V. Plaskeyev, and Ya M. Kolotyrykin, *Corrosion Science*, **19**, 343 (1979).
17. J. N. Wanklyn, *Corrosion Science*, **21**, 211 (1981).
18. R. D. Willenbruch, C. R. Clayton, M. Oversluizen, D. Kim, and Y. Lu, *Corrosion Science*, **31**, 179 (1990).
19. I. Olefjord and C. R. Clayton, *ISIJ International*, **31**, 134 (1991).
20. C. R. Clayton, G. P. Halada, and J. R. Kearns, *Materials*



- Science and Engineering*, **A198**, 135 (1995).
21. Y. C. Lu, C. R. Clayton, and A. R. Brooks, *Corrosion Science*, **29**, 863 (1989).
  22. K. Osozawa, N. Okata, Y. Fukase, and K. Yokota, *Boshoku Gijutsu*, **24**, 1 (1975).
  23. Y. S. Kim, *J. Corrosion Sci. Soc. of Korea*, **21**, 189 (1992).
  24. D. Kim, C. R. Clayton, and M. Oversluizen, *Materials Science and Engineering*, **A186**, 163 (1994).
  25. A. S. Vanini, J. P. Audouard, and P. Marcus, *Corrosion Science*, **36**, 1825 (1994).
  26. K. Osozawa, *Heat Treatment*, **36**, 206 (1996).
  27. A. R. Brooks, C. R. Clayton, K. Doss, and Y. C. Lu, *J. Electrochem. Soc.*, **133**, 2459 (1986).
  28. V. P. Yurkinski and E. G. Firsova, *J. Applied Chemistry of USSR*, **60**, 1944 (1987).
  29. E. G. Rozantsev, *Free Nitroxyl Radicals*, Plenum Press, NY (1970).
  30. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Co., Minnesota (1992).
  31. A. Rodes, R. Gomez, J. M. Perez, J. M. Feliu, and A. Aldaz, *Electrochimica Acta*, **41**, 729 (1996).
  32. S. Ye and H. Kita, *J. Electroanal. Chem.*, **346**, 489 (1993).
  33. A. Rodes, R. Gomez, J. M. Orts, J. M. Feliu, and A. Aldaz, *J. Electroanal. Chem.*, **359**, 315 (1993).
  34. A. Rodes, R. Gomez, J. M. Orts, J. M. Feliu, J. M. Perez, and A. Aldaz, *Langmuir*, **11**, 3549 (1995).
  35. R. Gomez, A. Rodes, J. M. Orts, J. M. Feliu, and J. M. Perez, *Surface Science*, **342**, L1104 (1995).
  36. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, NY (1986).
  37. D. E. Ibbotson, T. S. Wittrig, and W. H. Weinberg, *Surface Science*, **110**, 294 (1981).
  38. S. Sugai, H. Watanabe, H. Miki, T. Kioka, and K. Kawasaki, *Vacuum*, **41**, 90 (1990).
  39. S. Sugai, H. Watanabe, T. Kioka, H. Miki, and K. Kawasaki, *Surface Science*, **259**, 109 (1991).
  40. M. J. Breitschafter, E. Umbach, and D. Menzel, *Surface Science*, **109**, 493 (1981).
  41. V. K. Agrawal and M. Trenary, *Surface Science*, **259**, 116 (1991).
  42. T. J. Chun, in *Proceedings of 5<sup>th</sup> International Conference on Nuclear Engineering*, ICONE5-2030, May 26-30, Nice, France (1997).