Effects of Nitrogen on the Metastable Pitting and Repassivation Behavior of Austenitic Stainless Steels in Chloride Solutions

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Effects of nitrogen on the metastable pitting and repassivation behavior of 304L alloys in chloride solution were examined using the electrochemical noise analysis (ENA) and the scratching electrode technique. Results of ENA showed that the addition (0.1 wt%) of nitrogen to 304L alloy increased significantly the resistance to metastable pitting, which was confirmed by the appreciable decrease in the number of metastable pitting event simultaneously with the reduction in the intensity of the power spectrum density (PSD). Further, repassivation occurred much faster in the nitrogen added alloy than did in the alloy without nitrogen. These beneficial influences of nitrogen on the metastable pitting and repassivation behavior of austenitic stainless steels were discussed and rationalized based on the selective dissolution theory.

Keywords : *austenitic stainless steels, pitting, repassivation, nitrogen*

1. Introduction

It is well known that small amount of nitrogen improves significantly the resistance to pitting corrosion and mechanical properties of austenitic and duplex stainless steels in chloride solutions.[1,2] Before a stable pit occurs or at potentials active to pitting potential (E_{pit}), numerous metastable pits are reported to be formed on stainless steels. The metastable pits initiate and grow for a limited period before repassivation, and characterized by potential transients at open circuit or anodic current transient under potentiostatic condition. Since the metastable pit is a precursor to pitting corrosion, and may be developed into stable pits under certain conditions, metastable pitting on stainless steels and Al alloys have been extensively studied.[3-5] However, the influences of nitrogen on the metastable pitting behavior of stainless steels are rarely studied.

Repassivation is a film reforming process on the film broken surface, and hence its kinetics has been considered to be a critical factor in determining the susceptibility to SCC of an alloy.[6] Since the metastable pit exists before repassivation has completed at a film broken site, the metastable pitting behavior is thought to be influenced by the repassivation rate of an alloy. The research objective of the present work is to examine the influence of nitrogen on the metastable pitting behavior and repassivation kinetics of austenitic stainless steels in chloride solutions.

2. Experimental

Both 304L and 304LN were made by a vacuum induction melting (VIM) in order to examine the effects of N on the repassivation kinetics and metastable pitting behaviors of the alloys. Chemical compositions of the alloys are given in Table 1. The specimens were prepared by hot rolling and cold rolling processes to sheets 3 mm thick, and then solution annealed at 1050°C, followed by water quenching.

An electrochemical cell was devised to measure the repassivation current on the rapidly scratched surface of the alloys. The details in the cell were described elsewhere.[6,7] The surface of the sample was scratched under potentiostatic condition after a stable passive film had been formed, and current flow from the scratch was measured every millisecond during and after the scratching. Metastable pitting behaviors of the two alloys were examined by measuring anodic current transients of a specimen polarized to various applied potentials using a three electrode con-

Table 1. Chemical composition (wt%) of 304L and 304LN alloys.

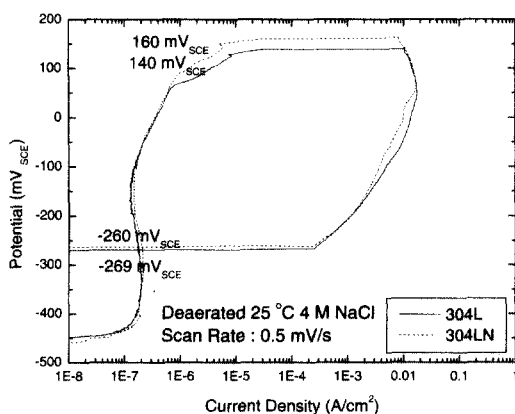|	C	Si	Mn	P	S	Cr	Ni	N
304L	0.017	0.40	1.05	0.014	0.001	18.97	9.98	0.01
304LN	0.011	0.51	1.05	0.014	0.001	18.94	10.00	0.10

ventional cell consisting of a specimen as a working electrode, saturated calomel reference electrode (SCE), and a platinum counter electrode.

The solutions used for scratch tests and metastable pitting test were, respectively, 4 M and 2M NaCl solutions deaerated with nitrogen purging. The specimens were cathodically cleaned at -1.0 V for 10 min to remove the air-formed film before all the experiments. All the potentials were referred to SCE.

3. Results and discussion

Figure 1 shows cyclic polarization responses for 304L and 304LN in deaerated 4 M NaCl solution at 25 C, where stable passivation occurs over a potential range from corrosion potential to 150 mV. Evidently, The Epit for 304LN is higher than that for 304L, which means that the resistance to pitting corrosion increased with N addition to 304L. However, the N addition to 304L did not greatly affect the overall cyclic polarization responses such as corrosion potential and repassivation potential except the E_{pit}.

Since repassivation occurs by a process of nucleation and growth of a passive film on the bare surface of an alloy, mechanisms proposed for the formation of a passive film can be applied to repassivation kinetics. Kwon et al.[6] showed repassivation occurred in two kinetically different processes; passive film initially nucleated and grew according to the place exchange mode[18] in which log i(t) is linearly proportional to q(t), and then grew according to the high field ion conduction mode[19] in which log i(t) is linearly proportional to the 1/q(t). Using these results, Kwon et al. demonstrated that the cBV, the slope in the log i(t) vs. 1/q(t) plot, is a quantitative measure of repassivation rate of passive film and closely associated with susceptibility to stress corrosion cracking of stainless steels

in a chloride solution.

Figure 2 shows a typical current transient curve for 304L when a scratch was made on the surface of the alloy polarized to a passive potential, -100 mV in a deaerated 4 M NaCl solution at 25°C. Once the passive film is broken by a scratch, the anodic current flowing from thescratch increases abruptly to a peak due to an anodic oxidation reaction, and thereafter decreases as repassivation pro-


Fig. 1. The cyclic polarization curves for 304L and 304LN in 25 °C, deaerated 4 M NaCl solution.

Fig. 2. (a) Current transient curve; (b) log i(t) vs. q(t); and (c) log i(t) vs. 1/q(t) plot for 304L in deaerated 25°C 4 M NaCl solution at 100 mV_{SCE}.

ceeds. Based on the data in Figure 2(a), the log i(t) vs. q(t) and the log i(t) vs. 1/q(t) plots were drawn and presented in Figure 2(b) and (c). Evidently, the repassivation of austenitic stainless steel occurred in consecutive processes with different kinetics: passive film initially nucleated and grew for about 10 ms according to the place exchange model, in which log i(t) was linearly proportional to q(t), and thereafter grew according to the high field ion conduction model from 10 to 100 ms, in which log i(t) was linearly proportional to 1/q(t). After 100 ms, the anodic current density, i(t), scattered over a small range of current density with a little increase in the charge density, q(t), probably due to reaching a steady-state.

Figure 3 (a) shows the current transient curves for 304L and 304LN upon scratching the surface of the alloys polarized to -100 mVSCE in a deaerated 4 M NaCl solution at 25°C. It is evident from Figure 2(a) that the peak current density of the current transient curve for 304L is higher than that for 304LN, demonstrating that the oxidation current of bare metal decreases by addition of 0.1 wt% N to 304L. The log i(t) vs. 1/q(t) plots was drawn based on the data of the current transient curves in Figure 3(a), and shown in Figure 3 (b). The value of cBV or

the slope of the linear region in the log I(t) vs. 1/q(t) plots, decreased significantly by the addition of nitrogen to 304L. According to the previous results reported by Kwon et al.,[6] the lower the value of cBV, the faster repassivated the alloy, thereby exhibiting less susceptibility to SCC.

Thus, a small amount addition of N to 304L increases
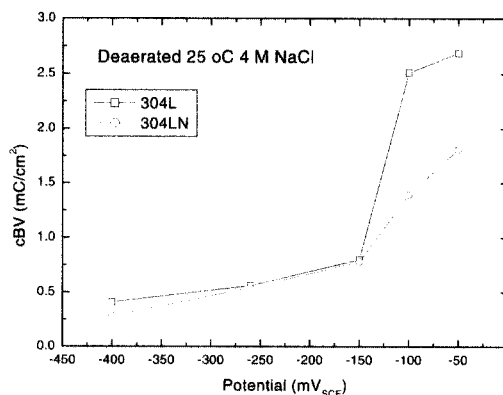
Fig. 4. Effect of applied potential on the value of cBV determined from the log i(t) vs. 1/q(t) plots for 304L and 304LN in deaerated 4 M NaCl at 25°C.

Fig. 3. (a) Current transient curve; (b) log i(t) vs. 1/q(t) plot of 304L and 304LN

Fig. 5. (a) Current transient curve; (b) PSD plot of 304L in deaerated 2 M NaCl at 80°C.

significantly the repassivation rate and hence SCC resistance of the alloy. Figure 4 shows the potential dependence of cBV values for the two alloys. At potentials active to -150 mV, the two alloys exhibit low and almost same value, demonstrating that the two alloys has fast repassivation rate and hence immune to SCC. In contrast, at potentials noble to -150 mV, the cBV values of the two alloys increased rapidly with applied potential. However, 304L showed much greater cBV value than did 304LN, exhibiting the slower repassivation rate compared with that of 304LN. This beneficial effect of nitrogen was more prominent with increasing applied potential.

Figure 5(a) shows a typical current transient curve for 304L at applied potential of -50 mV_{SCE} in a deaerated 2 M NaCl solution at 80°C. The current transient was measured during 2 h after the specimen immersed. Each current spike means an initiation and repassivation of metastable pitting. The number of current spikes per unit area was defined as metastable pitting event density. And, high value of metastable pitting event density means high susceptibility to metastable pitting.

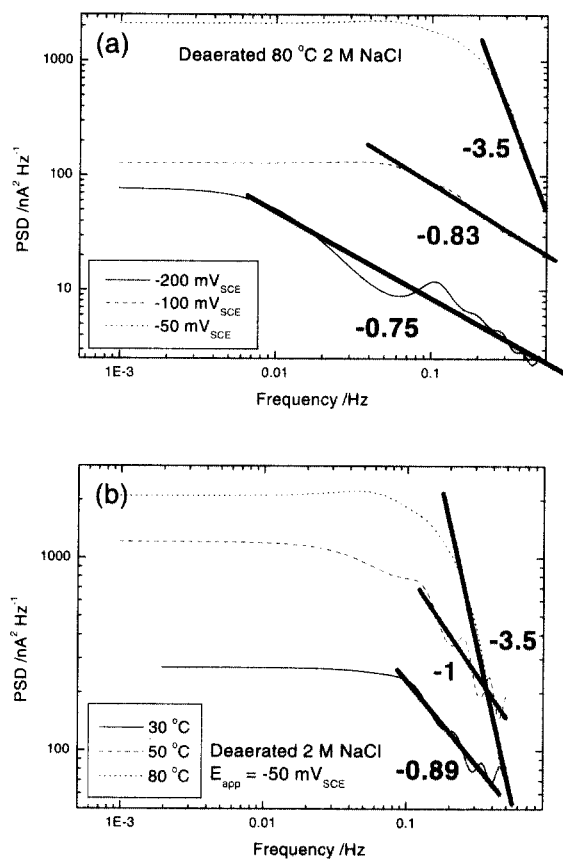Electrochemical noise such as current transient in Figure

5(a) have traditionally been analyzed in the frequency domain using power spectral density (PSD) plots. Two mathematical procedures used to convert signals in a time domain into frequency domain spectra are the fast Fourier transform (FFT),[10] and maximum entropy method (M EM).[11] Figure 5(b) shows PSD plots represented by FFT and MEM. Two important spectral parameters such as the intensity of PSD and the roll-off slope were suggested and reported to be related to the corrosion mechanisms.[12] In Figure 5(b), both MEM plot and FFT plot show high intensity of PSD in low frequency range, and the intensity of PSD decreases with increasing frequency. Therefore, the slope of the linear region in high frequency range or the roll-off slope, was observed. The higher the intensity of PSD in low frequency range, the higher the value of roll-off slope, the higher susceptibility to pitting is an alloy.[13]

A. Legat reported that the results of chaotic analysis indicated that the slope of PSD increases from passivation to localized corrosion.[14] Effects of applied potential and solution temperature on the intensity of PSD and the roll-off slope were examined using MEM, and shown
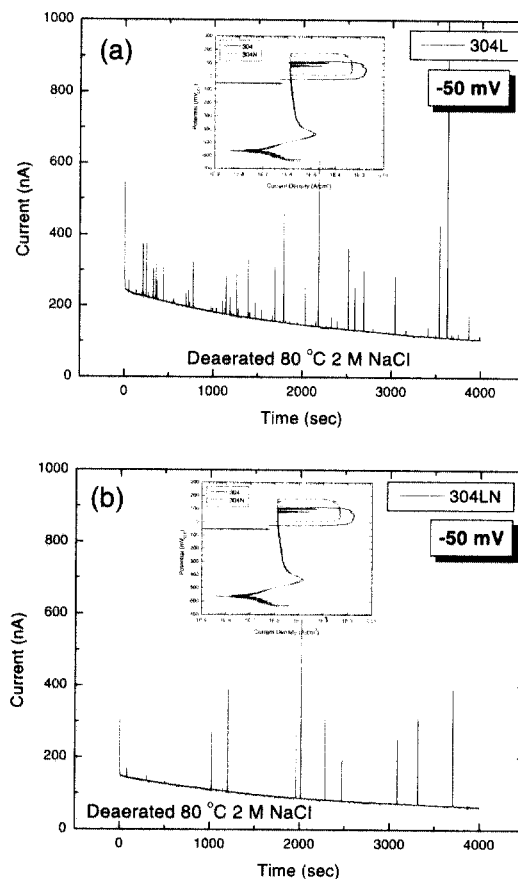

Fig. 6. Influence of (a) applied potential; (b) solution temperature on PSD plots.

Fig. 7. Current transients for (a) 304L; (b) 304LN in deaerated 80°C 2 M NaCl solution at 50 mVSCE
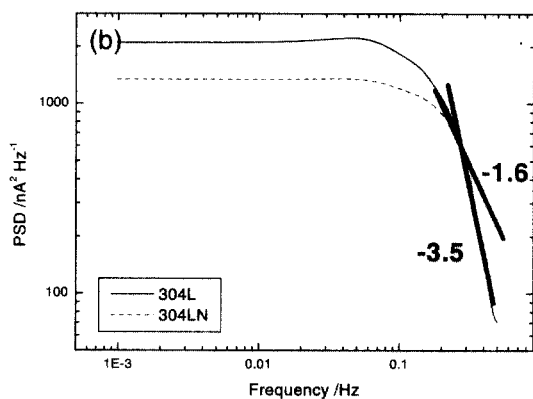
Fig. 8. PSD plots for 304L and 304LN in deaerated 80°C 2 M NaCl solution at 50 mVSCE.
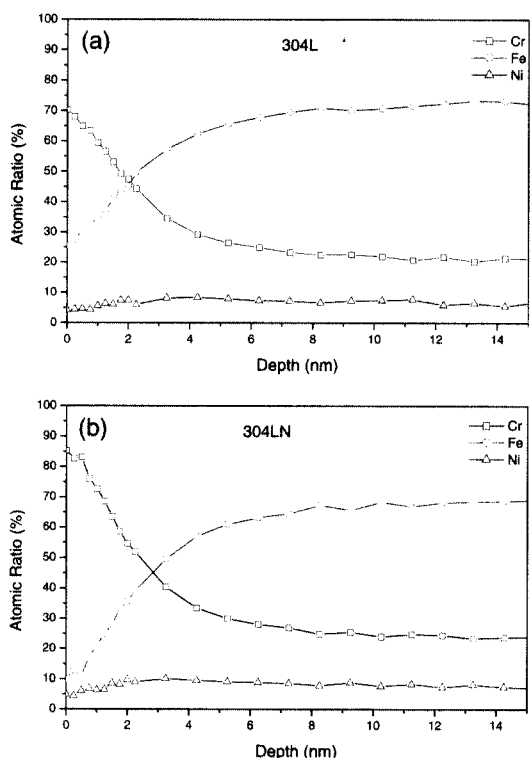

Fig. 9. In-depth composition profile of passive film formed on (a) 304L; (b) 304LN in deaerated 2 M NaCl at 80°C.

in Figure 6. It is evident that the intensity of PSD and the roll-off slope increased with increasing the applied potential and the solution temperature. Figure 6 suggests that the resistance of an alloy to pitting can be estimated by the intensity of PSD and the roll-off slope of PSD plot.

Figure 7 shows the current transients of 304L and 304LN at -50 mVSCE in 2 M NaCl solution at 80°C. Evidently, the number of current spikes and the current peak height of 304LN were much reduced compared with

those of 304L. Figure 8 shows the PSD plot drawn based on the current transients of the two alloys shown in Figure 7. Both the intensity of PSD and the roll-off slope decreased with N addition to 304L, suggesting that small amount of N improves the resistance to pitting.

There have been a lot of controversies on the influence of nitrogen alloying on the corrosion properties of stainless steels. Osozawa and Okato suggested the ammonia production theory in 1976,[15] and R. Bandy suggested the surface enrichment theory in 1985.[16] Figure 9 shows in-depth composition profiles of passive film formed on the two alloys. The XPS results demonstrate that Cr concentration in outer layer of 304LN is much higher than that of 304L. This suggests that a small amount of N promotes Fe-selective dissolution from passive film of the alloy, thereby forming a more protective Cr-enriched passive layer. The result is well corresponded with the selective dissolution theory claimed by Pawel.[1] Therefore, both the faster repassivation rate and the greater resistance to pitting corrosion of 304LN compared with those of 304L are due primarily to the formation of the nitrogen induced Cr-enriched passive film.

Conclusions

Effects of the N on repassivation kinetics and on the metastable pitting behaviors of 304L were evaluated using the scratching electrode technique and ENA, respectively. Conclusions drawn from this study are as follows:

1) Repassivation on the scratched surface of the alloys occurred in two kinetically different processes; passive film initially nucleated and grew according to the place exchange model in which log i(t) is linearly proportional to q(t), and then grew according to the high field ion conduction model in which log i(t) is linearly proportional to the 1/q(t).

2) By the addition of 0.1 wt% N to 304L, the repassivation rate evaluated by the cBV value was significantly increased at potentials noble to -150 mV in NaCl.

3) The intensity of PSD in low frequency and the roll-off slope of 304L were increased with increasing the applied potential and the solution temperature.

4) By the addition of 0.1 wt% N to 304L alloy, metastable pitting event density, intensity of PSD in low frequency, and the roll-off slope were decreased, suggesting that the alloy with N has higher resistance to pitting than the alloy without N.

5) Both the faster repassivation rate and the greater resistance to pitting corrosion of 304LN compared with those of 304L are due primarily to the formation of the nitrogen induced Cr-enriched passive film.

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