



Influence of HNO₃ treatments on the early stages of pitting of type 430 stainless steel

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Abstract

The effect of HNO₃ surface treatment on the early stages of pitting of Type 430 stainless steel has been studied by AC impedance method. At a given low potential, the Warburg impedance coefficient σ , which is calculated from impedance plots, is a maximum after wet polishing, and decreases with increasing HNO₃ concentration in the solution of surface treatment. It has been suggested that the surface becomes more passive and the most susceptible sites for pit nucleation are eliminated after HNO₃ treatments, and that increasing the HNO₃ concentration in treatment solution results in increasing the resistance of the steel to metastable pitting. The critical potential (E_m) at which metastable pit or pits start to grow on the surface of the steel depends on HNO₃ concentration in treatment solution. The higher the HNO₃ concentration in treatment solution, the higher the E_m values, showing that the nucleated pit or pits proceeding to metastable growth stage becomes more difficult. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

To ensure satisfactory service life, the surface condition of stainless steel must be given careful attention, because surface condition plays an important role in corrosion resistance. The effect of surface condition caused by various treatments such as wet polishing, dry polishing and HNO_3 treatments etc. on pitting corrosion of stainless steel has been studied by many researchers [1–7]. Sasaki and Burstein [6] measured the pitting potentials of Type 304 stainless steel polished by silicon carbide papers of different grit numbers. The relationship between the pitting potential, E_p , and grit number of silicon carbide paper was obtained. They pointed out that the pitting potential of stainless steel is lower for rougher surface than for smoother one. Recently, Burstein and Pistorius [2] focused on the effect of surface roughness on metastable pitting of stainless steel. The result indicated that the number of metastable pits (N) decreases with increasing grit number of silicon carbide paper at a given potential. They suggested that a smoother surface finish reduced the incidence of metastable pitting by substantially reducing the number of sites capable of being activated into metastable growth. In previous work [5], the authors discussed the effect of surface roughness on the critical potential of metastable pit or pits growing on the Type 301 stainless steel, E_m , and found that E_m relates with the change in grit number of silicon carbide paper. The higher the number of the silicon carbide paper, the higher the E_m value.

It is known that HNO_3 treatment is an effective method for increasing corrosion resistance of stainless steels [1,4,6,7]. The authors reported the effect of the chromium enrichment in the film formed by HNO_3 treatments on the corrosion resistance of Type 430 stainless steel [4]. It was also found that pitting potential, corrosion potential and polarization resistance increased with increasing chromium enrichment in the film formed by HNO_3 treatment. Barbosa and co-workers found that, for austenitic stainless steels, immersion in the nitric acid solution results in the removal of sulphide inclusion, thus eliminating the most susceptible sites for attack, leading to improved the resistance of pitting corrosion [6,7]. All of these results above indicate that pitting corrosion resistance of stainless steel increased by HNO_3 treatment.

The early stages of pitting are important for corrosion of stainless steel. It is also necessary to study the effect of HNO_3 surface treatments on the early stages of pitting. In the previous paper [8], the early stages of pitting on passivated Type 304 stainless steel in NaCl solution at low potentials in the passive region have been studied by AC impedance method. It was found that, for passivated stainless steel, there was a potential (E_m) below which the electrode reaction was under metal charge-transfer, and above which it was under both metal charge-transfer and diffusion. According to a recent theory about metastable pit growth of stainless steel in chloride solution, i.e. metastable pit growth of stainless steel is controlled by diffusion of metal cations in the perforated film on the surface of growing pit [10–12], E_m was estimated to be the potential at which metastable pit or pits start to grow on the steel [8].

In this paper, the AC impedance plot method is used to estimate E_m of Type

430 stainless steel with HNO₃ treatments. The early stages of pitting in the surface films formed by HNO₃ treatments have been studied, and the relationship between the early stages of pitting and HNO₃ concentration in treatment solution is discussed.

2. Experimental

The steel studied was a bright annealed Type 430 ferritic stainless steel, and the chemical composition is shown in Table 1. The specimens were cut into test pieces 50 mm long and 15 mm wide. The surface of specimens was treated by various methods summarized in Table 2.

The 3.5% NaCl test solution was prepared from distilled water with a specific electrical conductivity less than 2×10^{-6} S cm⁻¹ and reagent grade NaCl. The solution was de-aerated with high purity Ar before testing and kept under an Ar atmosphere during testing.

The AC impedance measurements were conducted from -230 mV towards the positive direction at intervals of 20 mV in 3.5% NaCl test solution for each specimen, and carried out after the specimens had been pre-passivated in the same solution for 30 min without application of potential to allow a uniform passive film formation on the surface. The impedance measurement was taken immediately after the potential was applied to a specimen. An impedance measurement system comprising a Potentiostat HA-501G (Hokuto Denko Ltd), PRE Analyzer S-5720C (NF ELECTRONIC INSTRUMENTS), and Computer (NEC) PC-9801 was used. A perturbation AC potential of amplitude 10 mV was applied over the frequency range from 0.5 mHz to 1 kHz.

The AC impedance measurements were performed at 25°C, and all potentials recorded in this paper were referred to the Saturated Calomel Electrode (SCE), and the counter electrode was untreated platinum sheet of dimensions 10 × 10 mm.

3. Results

Fig. 1 shows the Nyquist impedance plots of Type 430 stainless steel by wet-polished finally on silicon carbide paper of grit number 1000 measured at different low potentials in passive region in 3.5% M NaCl solution. It is found that the Nyquist impedance plot at -230 mV is a semicircle. When the potential increases above -210 mV, a diffusion tail begins to appear at low frequencies below

Table 1
The chemical composition of Type 430 stainless steel (mass%)

C	Si	Mn	S	Ni	Cr	P	N	Al
0.074	0.500	0.340	0.006	0.160	16.280	0.026	0.014	0.008

Table 2
Surface treatments of Type 430 stainless steel

Mark	Contents
WP	Wet polished with silicon carbide papers (# 400, 800, 1000)
WPN1	WP + passivation (dip in 1% HNO ₃ for 60 min at 50°C)
WPN10	WP + passivation (dip in 10% HNO ₃ for 60 min at 50°C)
WPN61	WP + passivation (dip in 61% HNO ₃ for 60 min at 50°C)

0.0007 Hz, and inclines at an angle of 45° to the *a*-axis. Thus it can be considered that the diffusion reaction has taken place on the passivated electrode at the potentials above –210 mV.

The Nyquist impedance plots of the other specimens shown in Table 2 in 3.5% NaCl solution at low potentials in the passive regions are given in Figs. 2–4. For each specimen, it can be observed that there are definite potentials above which the diffusion tail appears on the Nyquist impedance plots, i.e. –170 mV (WPN1), –130 mV (WPN10) and –110 mV (WPN61). In each of these cases, one modification which takes into account diffusion processes at the electrode is modeled by the inclusion of a Warburg impedance (Z_w). Z_w is defined according to Eq. (1).

$$Z_w = \sigma \omega^{-1/2} (1 - j) \quad (1)$$

Where σ is the Warburg impedance coefficient (ohm s^{1/2}) and $\omega = 2\pi f$ (rad s⁻¹).

The Warburg impedance coefficients σ can be obtained from Eq. (2) by using the Nyquist impedance plots of Figs. 1–4 at low frequencies where the diffusion tails are inclined at angles of 45° to the *a*-axis as shown in Fig. 5 [9].

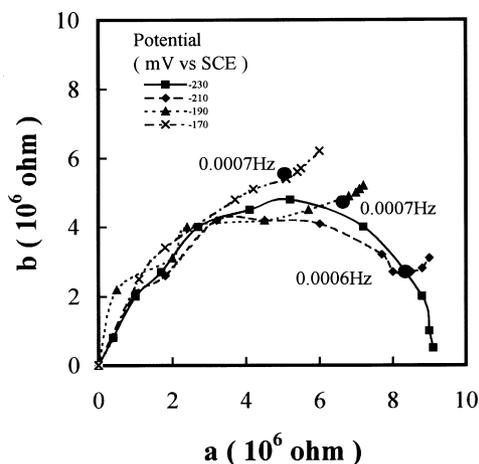


Fig. 1. Nyquist impedance plots of WP at different low potentials (● diffusion tail begins to be inclined at an angle of 45° to the *a*-axis).

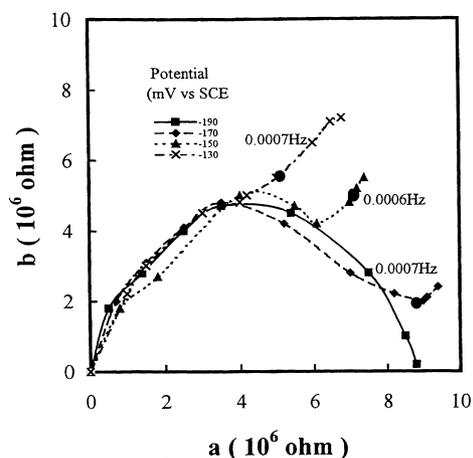


Fig. 2. Nyquist impedance plots of WPN1 at different low potentials (● diffusion tail begins to be inclined at an angle of 45° to the *a*-axis).

$$\sigma = b\omega^{1/2} \tag{2}$$

In Eq. (2) *b* is the reactive component of impedance (ohm) at which the diffusion tail begins to be inclined at an angle of 45° to the *a*-axis, $\omega = 2\pi f$ (rad s⁻¹), i.e. *f* is a frequency at which the diffusion tail begins to be inclined at an angle of 45° to the *a*-axis.

The values of σ for the Type 430 stainless steel with different surface treatments are shown in Table 3.

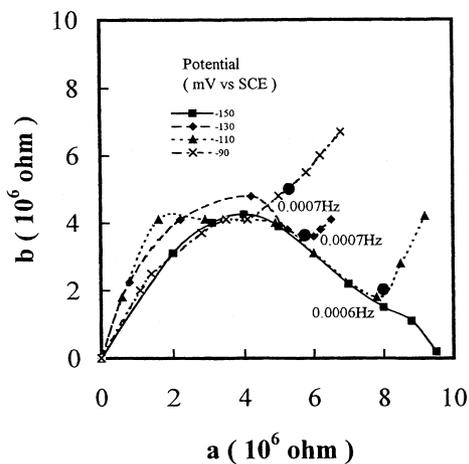


Fig. 3. Nyquist impedance plots of WPN10 at different low potentials (● diffusion tail begins to be inclined at an angle of 45° to the *a*-axis).

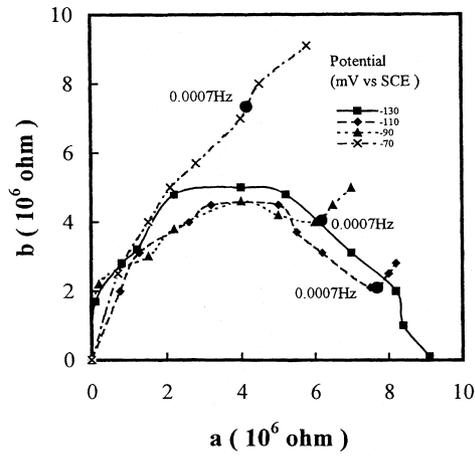


Fig. 4. Nyquist impedance plots of WPN61 at different low potentials (● diffusion tail begins to be inclined at an angle of 45° to the a -axis).

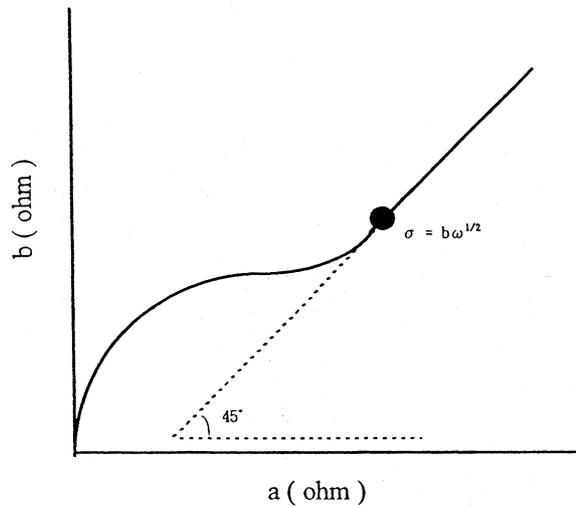


Fig. 5. Calculation of σ from Nyquist impedance plots.

4. Discussion

It has been suggested that there are two consecutive stages before stable pit grow, i.e. when the potential is below the pitting potential [10–12]. The first stage is pit nucleation, and the second is growth of metastable pits. Pit nucleation is considered to be a metal charge transfer process, and growth of metastable pit is

Table 3
The values of σ (kohm s^{1/2}) for Type 430 stainless steel with different surface treatments

Potential mV vs SCE	WP σ	WPN1 σ	WPN10 σ	WPN61 σ
-230	0	0	0	0
-210	120	0	0	0
-190	290	0	0	0
-170	360	140	0	0
-150	–	250	0	0
-130	–	340	110	0
-110	–	–	240	80
-90	–	–	370	170
-70	–	–	–	280

suggested to be controlled by diffusion with a perforated film over the mouths of the pit. Therefore, at the potential below the pitting potential, the early stages of pitting corrosion can be detected by observing the reaction of the electrode [8,13,14]. If the electrode reaction is only metal charge-transfer, it can be considered that the stage of pitting corrosion belongs to pit nucleation. If the electrode reaction contains both metal charge-transfer and diffusion, the stage of pitting corrosion has entered metastable pitting growth. The growth of metastable pits on the surface depends on the maintenance of effective diffusion provided by the perforated films over the mouths of these pits [10–12]. According to the result obtained by Hunkeler et al. [16] the passivated film is unstable above E_{sf} (the critical potential for salt film formation, i.e. -190 mV (SCE) for AISI 301SS), and tends to be replaced by a salt film [15]. The films which are formed on the mouths of the pits are considered as salt films [16–18]. In this work, the Warburg

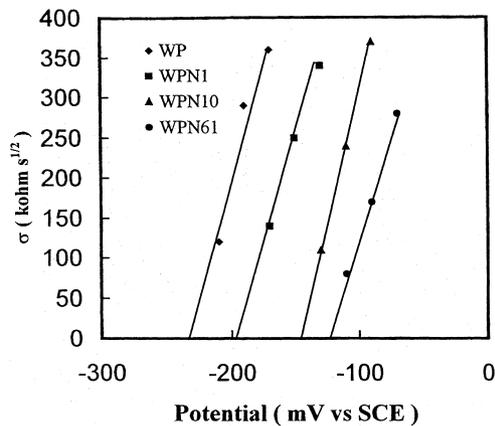


Fig. 6. Relationship between the potential and the Warburg diffusion coefficient (σ) in 3.5% NaCl solution for Type 430 stainless steel with various surface treatments.

impedance coefficient, σ , is introduced to represent the resistance coming from the diffusion process within the salt films.

Fig. 6 shows that the relationship between the potential and σ in 3.5% NaCl solution for Type 430 stainless steel with various surface treatments. It is found that the value of σ increases with increasing potential for each of the specimens. This behavior has been suggested to originate in the thicker salt films on the electrode at the higher potentials [8,13,14]. Fig. 6 also shows that σ is a maximum after wet polishing, and decreases with increasing HNO_3 concentration in treatment solution at a given potential. According to previous works [1,3,4,7,19], it has been suggested that the surface becomes more passive and the most susceptible sites for pit nucleation are eliminated after HNO_3 treatments. This is because the chromium is enriched [1,4] and the sulphide inclusions [3,7,19] are removed during the HNO_3 treatments. The authors used AES to detect the chromium concentration in the surface of the film formed on Type 430 stainless steel with different surface treatments [4]. It was found that the total amount of the chromium concentration is the lowest after wet grinding, and increases with increasing HNO_3 concentration in the treatment solution. Increasing chromium concentration in passive film may suppress anodic dissolution. So the active surface sites available for metastable pits on the electrode at a given potential decreases with increasing the chromium concentration in the film. Since the metastable pits continue to survive depending on the maintenance of effective diffusion provided by the salt films over the mouths of these pits, decreasing the metastable pits on the surface results in decreasing the films on these pits. This means that the diffusion barriers provided by the salt films decreases with increasing chromium concentration in the surface film, therefore, leading to

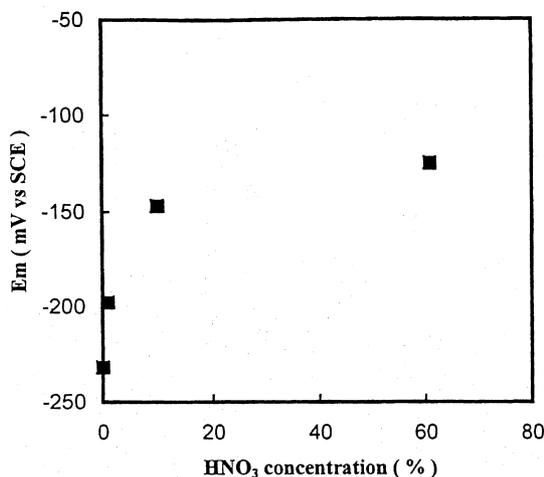


Fig. 7. Relationship between HNO_3 concentration in treatment solution and E_m for Type 430 stainless steel.

smaller σ . In other words, σ decreases with increasing HNO_3 concentration in treatment solution. The lines through the points which are measured for WP, WPN1, WPN10, WPN61 in 3.5% NaCl solutions intersect the potential axis at -232 , -198 , -147 and -125 mV as shown in Fig. 6. This means that extrapolated potentials for zero σ for WP, WPN1, WPN10 and WPN61 are at -232 , -198 , -147 and -125 mV, respectively. In other words, above -232 , -198 , -147 and -125 mV, the diffusion processes begin to appear on the surfaces of WP, WPN1, WPN10 and WPN61, respectively. Therefore, these potentials can be considered as critical potentials, E_m , at which metastable pit or pits start to grow on the surfaces of the specimens by respective treatments [8,13,14]. The relationship between the HNO_3 concentration in the treatment solution and E_m is shown in Fig. 7. It can be found that E_m is a minimum after wet grinding, WP, and increases with increasing HNO_3 concentration in the solutions ($E_{m(\text{WPN1})} < E_{m(\text{WPN10})} < E_{m(\text{WPN61})}$). This implies that E_m depends on HNO_3 concentration in the treatment solution. Because increasing HNO_3 concentration in treatment solutions leads to an increase in chromium concentration and probably accelerates elimination of sulphur inclusion in the surface film, the anodic dissolution and the available sites for pit nucleation become lower and less, respectively, at higher potentials. The transition to metastable pitting may thus be hampered, resulting in higher E_m . The higher the HNO_3 concentration in the treatment solution, the higher the E_m values, showing that the nucleated pit or pits proceeding to metastable growth stage becomes more difficult.

5. Conclusions

From results obtained with Type 430 stainless steel subjected to surface treatments in various HNO_3 solutions, the following conclusions are drawn.

1. At a given low potential in the passive region, the Warburg impedance coefficient is a maximum after wet polishing, and decreases with increasing HNO_3 concentration in the solution for passivation treatment. This fact implies that increasing the HNO_3 concentration in the treatment solution results in increasing the resistance of the steel to metastable pitting.
2. The critical potential, E_m , for metastable pitting growth correlates with the HNO_3 concentration in the treatment solution. E_m increases with increasing the HNO_3 concentration in treatment solution.

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