

Comparison of Repassivation Kinetics of Stainless Steels in Chloride Solution

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Using a rapid scratching electrode technique, the repassivation kinetics of type 304, 316, 444, and 2205 stainless steels (SS) were investigated in a chloride solution. The value of cBV in a $\log i(t)$ versus $1/q(t)$ plot as an effective measure of the repassivation rate was used to compare the repassivation behaviors among the alloys. During repassivation, lower values of cBV for SS corresponded with faster repassivation rates with the formation of a more protective passive film. In a comparison of repassivation rates based on the alloy's cBV values, the best repassivation behavior was shown by 2205 SS, followed by 444 SS and 316 SS. However, 304 SS exhibited an inflection point in the $\log i(t)$ versus $1/q(t)$ curve, suggesting that dissolution by localized corrosion rather than SCC may occur in the alloy under given conditions.

Keywords: stainless steels, repassivation kinetics, scratching electrode, passive film

1. INTRODUCTION

Stress corrosion cracking (SCC) of stainless steels in chloride solution occurs as a result of a repetitive process of film breakdown, dissolution, and repassivation [1]. Repassivation is a film reforming process on the broken surface film, and repassivation kinetics is therefore considered a critical factor in determining the SCC susceptibility of an alloy [2,3].

Cabrera and Mott suggested a high-field ion conduction model in which the passive film grows by the transport of metal ions across the film toward the film-solution interface under high electric fields of a few megavolts per centimeter [4]. Using this model as a basis, Burstein and Marshall used a scratch electrode technique to demonstrate that $\log i(t)$ is linearly proportional to $1/q(t)$ with a slope of cBV, where $i(t)$ is the anodic current density that flows from the scratch, $q(t)$ is the charge density that flows from the scratch, c is a constant for the alloy, B is a constant related to the activation energy barrier for ion movement, and V is the potential difference across the passive film [5].

Furthermore, Kwon *et al.* reported that the value of cBV is an effective measure of both the repassivation rate and the protectiveness of the reformed film and, hence, can be used as a parameter associated with SCC susceptibility [6,7]. Specif-

ically, for a given alloy-environment system, the lower the value of the cBV, the faster the repassivation of the alloy. This faster repassivation is achieved through the formation of a thinner and more protective film that exhibits less SCC susceptibility. The value of the cBV was found to be very sensitive to the applied potential, the Cl^- concentration, and the solution temperature [6]. Kwon *et al.* also successfully demonstrated the role of alloying elements such as Cr, Mo, W, and Ni on the repassivation behavior of Fe-based alloys, and found good agreement with SCC behavior in the existing literature [7,8].

Stainless steels (SSs) are classified as ferritic (α), austenitic (γ), and duplex ($\alpha+\gamma$), depending on the microstructure. The microstructure is determined by the major constituents such as Cr, Mo, W, Ni, and N. Among these constituents, Cr, Mo, and W act as a ferrite former and Ni and N act as an austenite former. The most popular stainless steels used in structural parts, particularly parts for which SCC resistance is required such as in a hot water tank, are type 304 and 316 austenitic stainless steels, type 444 ferritic stainless steels [9], and type 2205 duplex stainless steel. Thus far, however, the SCC resistance of these alloys has seen little investigation in terms of repassivation kinetics.

The objective of the present work is to compare the repassivation kinetics of commonly used austenitic, ferritic, and duplex stainless steels in a chloride solution by measuring their cBV values.

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Table 1. Chemical compositions (wt.%) of the alloys used

	Cr	Ni	Mo	Mn	Si	N
304	18.4	8.2	-	1.0	0.6	-
316	16.8	10.3	2.1	1.1	0.6	-
444	18.4	-	2.0	0.2	0.2	-
2205	22.5	5.6	3.1	1.5	0.5	0.17

2. EXPERIMENTAL PROCEDURE

For the materials, we used 1 mm thick, mill-annealed stainless steel sheets of type 304, 316, 444, and 2205, all of which were supplied by POSCO. Table 1 shows the chemical compositions of the alloys.

A cell, in conjunction with the rapid scratching electrode technique, was devised to measure the repassivation current of the alloys. The cell consisted of a specimen as a working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE) positioned in a salt bridge with a high silica tip. An alumina tip loaded on a spring was pulled along the surface of the specimen by an air-pressured cylinder connected to a solenoid valve so as to rupture the surface film by making a scratch. The duration of the alumina tip's contact with the surface of the specimen during the scratching process was $< 1 \mu\text{s}$. A schematic of the cell system has been presented elsewhere [6,7]. The surface of the sample was scratched under a potentiostatic condition after a stable passive film had been formed. Current flow during and after the scratching was measured every millisecond and computer-processed for further analysis. To examine the passive behavior of the alloy, an anodic polarization test was conducted at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$. All the tests were performed at 50°C in a 4 M NaCl solution deaerated with nitrogen. All the electrochemical potentials were referred to SCE.

3. RESULTS AND DISCUSSION

Fig. 1 shows the anodic polarization responses of type 304, 316, 444, and 2205 stainless steels (SS) in 4 M NaCl solution at 50°C . From the curves, the pitting potential, as a measure of resistance to pitting corrosion, of 304, 316 and 444 SS was determined to be 40, 110, and 115 mV, respectively. 2205 SS, exceptionally, did not exhibit pitting corrosion. The increase in current density near 1000 mV for this alloy is due to an oxygen evolution reaction rather than pitting. The pitting resistance of SS is often estimated on the basis of its pitting resistance equivalent ($\text{PRE} = \% \text{Cr} + 3.3 \% \text{Mo} + 16 \% \text{N}$), which reflects the contributions of major alloy constituents of Cr, Mo, and N to the pitting resistance. The calculated PRE for 304, 316, 444, and 2205 SS are 18.4, 23.73, 25, and 35.45, respectively. This appears to coincide roughly with the pitting potential measurement results.

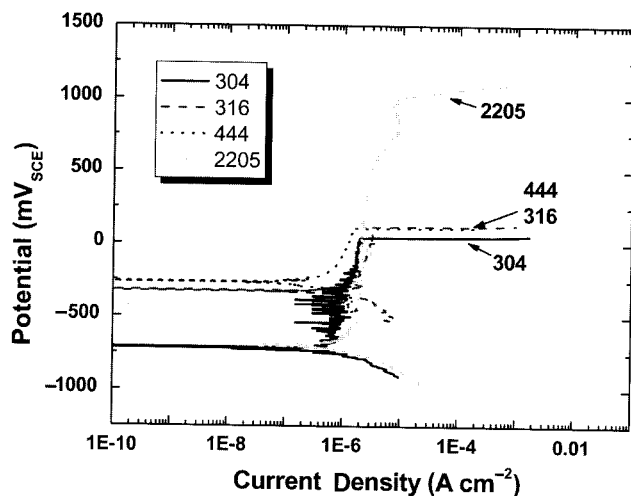


Fig. 1. Anodic polarization responses of type 304, 316, 444, and 2205 SS in 4 M NaCl solution at 50°C .

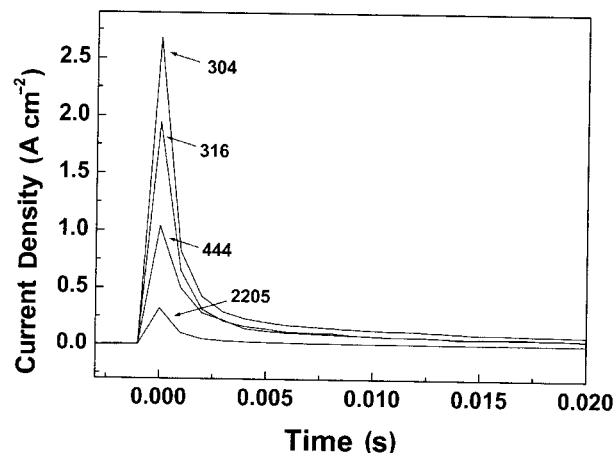


Fig. 2. Current transient curves on the scratched surface of 304, 316, 444, and 2205 SS in a 4 M NaCl solution at 50°C .

Fig. 2 shows the current transient curves measured by scratching the surface of the alloys polarized to -200 mV in a deaerated 4 M NaCl solution at 50°C . The applied potential of -200 mV was selected because at that value all the alloys exhibited passive behavior in the test solution, as shown in Fig. 1. Once the passive film was broken by the scratch, the anodic current flowing from the scratch increased abruptly to a peak due to an anodic oxidation reaction. The current then decreased as the repassivation proceeded. The peak current density became smaller in the following order: 304, 316, 444, and 2205 stainless steel (SS). The repassivation rate of an alloy can be compared with respect to the repassivation time required to achieve a predetermined degree of repassivation from scratching [6]. As the repassivation time is decreased, the repassivation rate increases accordingly. Fig. 2 shows that 2205 SS can be repassivated to a predetermined degree of repassivation (i_r) much more quickly than other alloys.

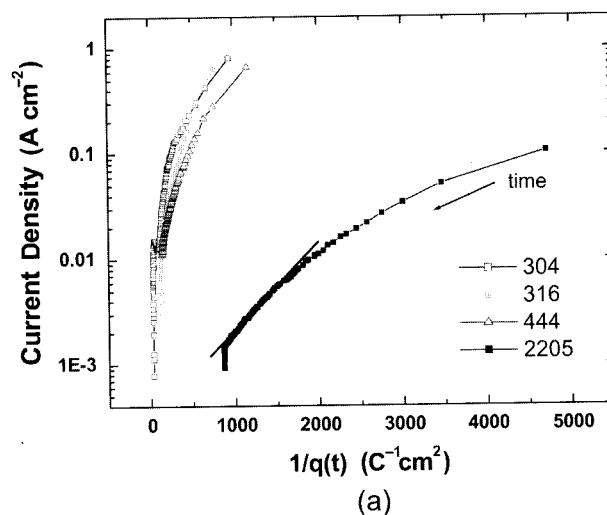
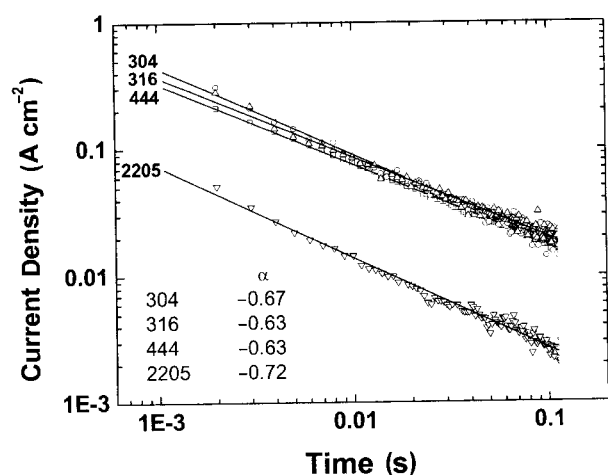


Fig. 3. The log $i(t)$ versus log t plots for 304, 316, 444, and 2205 SS, obtained from the current transients curves.

As shown in Fig. 3, the decay of current density on the scratched surface follows an empirical law in which $i(t) = a \cdot t^{-\alpha}$ [10]. The decay gradients (α), which are determined by the slopes of the log $i(t)$ versus log t curves, were 0.67 to 0.72. According to the high field ion conduction model, this value is less than 1 [11]. However, the value appears to be independent of alloy type. Thus, the a value does not appear to accurately reflect the repassivation rate of the alloys.

Based on the $i(t)$ versus t curves in Fig. 2, the charge flow $q(t)$ due to the scratching of the surface was calculated as described elsewhere [6]. Since repassivation occurs by the nucleation and growth process of the passive film on the bare surface of the alloy, the mechanism proposed for the formation of a passive film can be applied to the repassivation kinetics. The repassivation behavior of SS has been interpreted by several researchers on the basis of the high field ion conduction model, [6,7,12] in which log $i(t)$ is linearly proportional to $1/q(t)$.

Accordingly, log $i(t)$ versus $1/q(t)$ plots were drawn according to Eq. 1, and presented in Fig. 4.

$$\log i(t) = \log A + \frac{cBV}{q(t)} \quad (1)$$

where c is $zF\rho/2.3M$, which can be assumed to be constant for SS ($z=3$, $\rho=5.24 \text{ g}\cdot\text{cm}^{-3}$), and V is the potential drop across the film thickness h . A and B are constant parameters associated with the activation energy of the mobile ion in the film. Details of the other parameters can be found elsewhere [6].

In Fig. 4, at the initial stage of repassivation, the log $i(t)$ is linearly proportional to $q(t)$ and thus deviates from the linearity, where passive film nucleated and grew. log $i(t)$ then has a linear relationship with $1/q(t)$ in the intermediate stage, except for log $i(t)$ of 304 SS. In this stage, passive film grew according to the high field ion conduction model. At the final stage, the anodic current density, $i(t)$, scattered over a

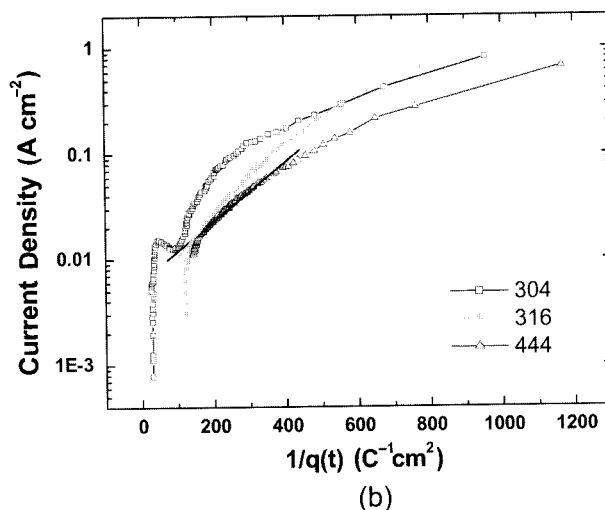


Fig. 4. The log i versus $1/q(t)$ plots for 304, 316, 444, and 2205 SS (a) and rescaled comparison among 304, 316, and 444 SS (b).

small range of current density with a slight increase in the charge density, $q(t)$. This phenomenon is presumably due to reaching a steady state.

From the log $i(t)$ versus $1/q(t)$ curves in Fig. 4, the cBV values were determined to be 0.004 for the 316 SS, 0.002 for the 444 SS, and 0.0008 for the 2205 SS. For 304 SS, an inflection point appeared in the curve. This indicates that stable localized corrosion propagated after scratching the surface in these test conditions. We confirmed this phenomenon in a previous work in which 304 SS exhibited severe dissolution via pitting in a deaerated 4 M NaCl solution at 50°C with an applied potential of -200 mV [6]. Compared to other alloys, 2205 SS had a significantly lower cBV value. This indicates that 2205 SS repassivates rapidly when the protective film reforms after the film breaks down. It therefore has good resistance to SCC. Due to the large difference in cBV values between 2205 SS and other alloys, the cBV values of 304, 316, and 444 SS were separately compared, as shown in

Fig. 4(b). The cBV of 444 SS was slightly higher than that of 316 SS. The lower cBV indicates the higher repassivation rate that is necessary to prevent SCC.

The repassivation kinetics of stainless steels appear to be associated with their alloying constituents. It is generally agreed that the alloying elements Cr, Mo, and N increase the protectiveness of passive film, and thereby localize corrosion resistance in stainless steels [13]. It was previously found that the cBV decreases with an increase in Cr and Mo in Fe-29Cr alloys [7]. The beneficial effects of N on repassivation kinetics and SCC susceptibility have also been reported [14]. However, the effects of Ni on SCC susceptibility and repassivation kinetics remain controversial. According to the Copson diagram, which indicates the effect of Ni content on SCC susceptibility of 18~20 % Cr SS, the SCC resistance reaches a minimum at 8~12 % Ni; the SCC resistance then increases as Ni content moves away from the minimum [15]. This diagram is often used to explain the relatively poor SCC resistance of 18Cr-10Ni 304 SS. However, as suggested elsewhere, the effect of Ni on the SCC resistance of stainless steels can also be understood as an aspect of repassivation kinetics [8].

5. CONCLUSIONS

The repassivation kinetics of 304, 316, 444, and 2205 SS were compared on the basis of a high field ion conduction model. The value of cBV in the region that shows a linear relationship between $\log i(t)$ and $1/q(t)$ is a quantitative measure of the repassivation rate. During repassivation, as the value of cBV for SS is lowered, the repassivation rate increases accordingly with the formation of a more protective passive film. Comparing the repassivation rates of the tested alloys on the basis of their cBV values, the best repas-

sivation behavior is shown by 2205 SS, followed by 444 SS and 316 SS. However, 304 SS shows an inflection point in the $\log i(t)$ versus $1/q(t)$ curve, suggesting that the alloys may experience dissolution by pitting in the given test conditions.

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