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Detection of Pitting on Cast Iron with AC Impedance Spectroscopy

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The pitting behavior of high-chromium cast iron has been studied with AC impedance spectroscopy. When impedance measurements are carried out at open circuit potentials, it is observed at the initial stage of pitting that with increasing time, the polarization resistance R decreases for the better pitting resistant specimen, and increases for the poorer one. However, when the electrode potential is suitably fixed during the measurements, the R value shows an abrupt decrease at the initial stage for the sample with a poorer pitting resistance. This large change in the R value indicates the initiation of the pitting process and thus can be used for detecting such onset.

It is of significant importance in practical applications to develop methods which can be used to detect the initiation of pitting, especially in a nondestructive manner. It has been shown recently that AC or electrochemical impedance spectroscopy could be used for such a purpose. Mansfeld and co-workers[1–3] demonstrated that the pitting of aluminum-based alloys in chloride media could be detected by the characteristic changes in the low-frequency region of the impedance spectra. They reported that during the pitting process, the capacitance values were increased tremendously but the polarization resistance did not appear to change significantly. Oltra and Keddam[4] proposed an impedance network which modeled the pitting process. In the light of these works, we have used AC impedance spectroscopy to study the pitting behavior of high-chromium cast iron in 3% NaCl solution, and we find that the impedance measurements at fixed potentials can be used to detect the onset of the pitting process on high-chromium cast iron. This paper provides an account of our findings.

Experimental

Two specimens, called Specimen A and Specimen B, of self-prepared high-chromium cast iron were used in this study. Specimen A contained 2.86% C, 0.037% P, 0.049% S, 0.87% Cu, 1.14% Mo, 0.26% Mn, 0.44% Si, and 17.02% Cr, whereas Specimen B contained 2.36% C, 0.053% P, 0.013% S, 0.15% Cu, 0.10% Mo, 0.26% Mn, 1.30% Si, and 39.4% Cr.[5] All reagents used were of analytical grade. High-chromium cast iron electrodes (both Specimens A and B) with a surface area of 1 cm^2 were abraded successively with emery papers No. 2, 3, 4, 5, and 6, then washed and degreased with acetone, dried and rinsed with deionized water, and finally immersed in 3% NaCl solution (pH 6) at 25±0.5 °C in an electrochemical cell. Impedance experiments were performed in a three-electrode electrochemical cell with a Pt electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, over a frequency range of 0.05 Hz—100 kHz. The measurements were made with a PARC M273 potentiostat, and a 5208 EC lock-in analyzer interfaced with an IBM PC/XT computer and a PARC software system.

Results and Discussion

Figure 1(a) and (b) show the Nyquist plots for Specimens A and B, respectively, after they were immersed in

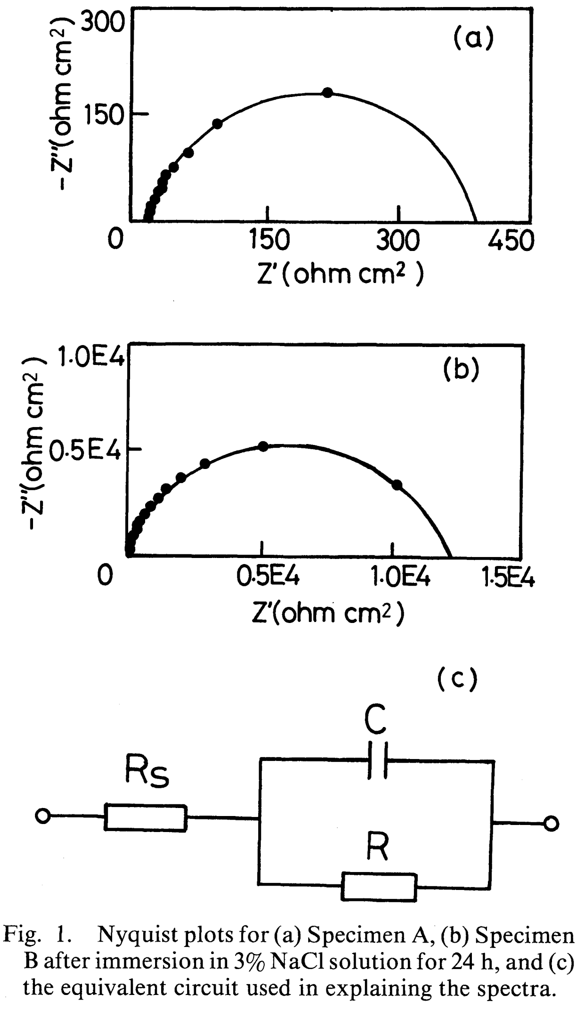

Fig. 1. Nyquist plots for (a) Specimen A, (b) Specimen B after immersion in 3% NaCl solution for 24 h, and (c) the equivalent circuit used in explaining the spectra.

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3% NaCl solutions for 24 h. The surface appearance of the immersed samples indicated that both specimens had undergone pitting attack, with a more severe one occurring on Specimen A. As only a single time constant is obtained for both specimens, the spectra can be explained by an equivalent circuit as shown in Fig. 1(c), where R_s represents the solution resistance, C the parallel combination of capacitances of passive and pitted areas, and R the parallel combination of the resistances of the passive and pitted areas. The R_s and R values can be measured from the Nyquist plots,[6] and the C value is calculated according to

$$C=\frac{1}{2\pi f_{\theta,\max}|z|_{\theta,\max}}\ ,$$

where $f_{\theta,\max}$ is the corresponding frequency value and $|z|_{\theta,\max}$ is the impedance modulus value at the maximum phase angle $\theta_{\max}$, in the Bode plot.[7]

For Specimens A and B, the R values were found to be 3.9×10^2 and $1.2\times10^4\,\Omega$, respectively, and the C values were 5.04×10^{-3} and 6.7×10^{-5} F cm^{-1}, respectively, after 24 h of immersion in 3% NaCl solution. The differences in the R and C values between Specimens A and B are about two orders in magnitude and which can be rationalized as follows. The pitted area becomes larger with increasing number and depth of pits, and hence the passsive area becomes smaller. Because the resistance for the pitted area is much smaller than that of the passive area,[2] it follows that the R value is decreased and the C value is increased after the pitting attack. Hence, it is concluded that Specimen B has a much better pitting-corrosion resistance than Specimen A.

Detailed pitting behavior of Specimens A and B in 3% NaCl solution can be seen from the results discussed below. Figure 2 shows the Nyquist plot for Specimen A during immersion in 3% NaCl solution at various times. The measurements are taken at open-circuit potentials. Curves (a), (b), (c), (d), and (e) correspond to the immersion times of 5 min, 15 min, 30 min, 6 h and 48 h, respectively. The polarization resistance R rises quickly at the initial stage of pitting (curves (a), (b), and (c)) but becoming steady after 6 h of immersion (curves (d) and (e)). As Specimen A has a rather poor resistance to pitting-corrosion, pitting develops rapidly once it is immersed in the solution, and the corrosion potential E_{corr} quickly moves from -0.48 V (curve(a)) to -0.59 V vs. SCE (curve (c)) within 30 min. Using the program of PARC M378 software system, it took about 10 min to complete the measurement of the spectrum in the frequency range of 0.05 Hz—100 kHz, and during this 10-min period the electrode potential was maintained at the initial potential of the measurement. As E_{corr} moves to a more negative value, the electrode becomes anodically polarized during the 10-min period and hence the anodic current determines the R values. Figure 3 shows the plots of E_{corr} and C vs. the immersion time for Specimen A in 3% NaCl solution. The corrosion potential E_{corr} drops rapidly at the beginning. The abrupt drop in E_{corr} within 30 min of immersion has resulted in a stronger polarization on the electrode, causing the R values to become smaller (curves (a), (b), and (c) in Fig. 2).The R value is the smallest at 5 min of immersion (curve (a)). After 6 h of immersion, E_{corr} rises slightly and finally becomes steady. The reason for this slight increase in E_{corr} is probably that the pits are covered and filled with the corrosion products after a period of immersion. The C value, on the other hand, steadily increases with the time of immersion as shown in Fig. 3. This may be attributed to an increase in the pitted area during the pitting process, in addition to the

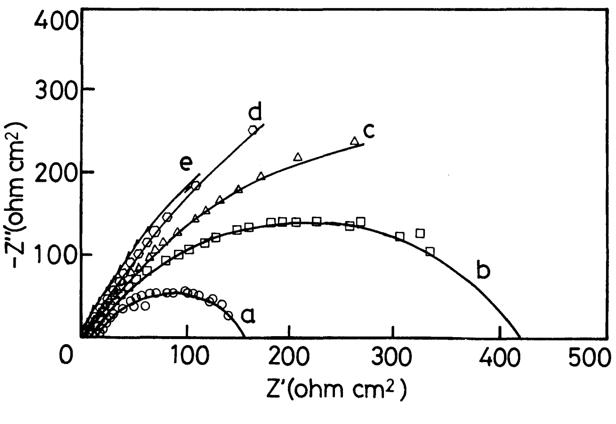

Fig. 2. Nyquist plots for the Specimen A during immersion in 3% NaCl solution for various times and at the open-circuit potential. Curves a (○), b (□), c (△), d (○), and e (/) correspond to the immersion times of 5 min, 15 min, 30 min, 6 h, and 48 h, and the corrosion potentials of −0.48, −0.52, −0.59, −0.59, and −0.56 V, respectively.

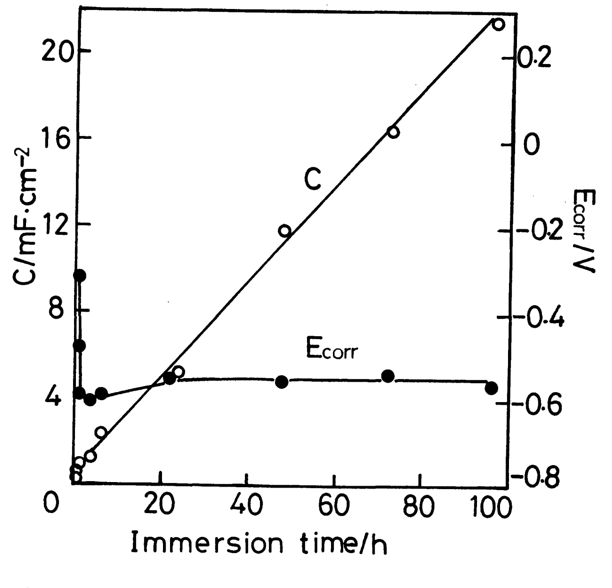

Fig. 3. Plots of corrosion potential E_{corr} (●) and capacitance C (○) vs. the immersion time in 3% NaCl solution for the Specimen A at the open-circuit potential.

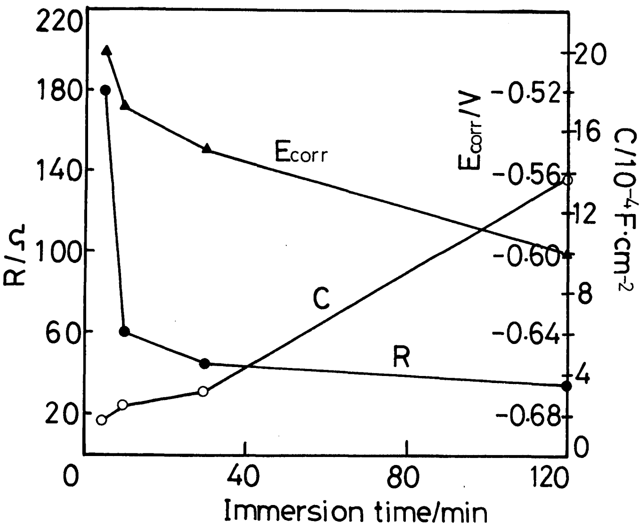

Fig. 4. Plots of corrosion potential E_{corr} (▲), capacitance C (○), and polarization resistance R (●) vs. the immersion time in 3% NaCl solution for the Specimen A at the fixed potential of −0.5 V (SCE).

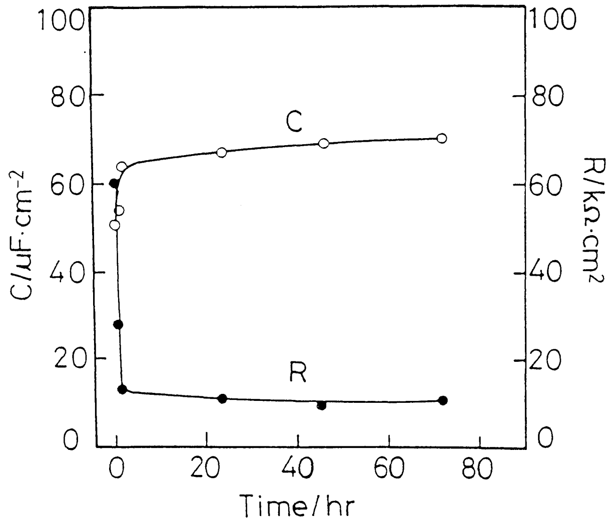

Fig. 5. Plots of capacitance C (○) and polarization resistance R (●) vs. the immersion time in 3% NaCl solution for the Specimen B at the open-circuit potential.

thickening of the salts films or corrosion products in the pits.[2)]

When the impedance measurements are carried out at a suitably fixed potential instead of the open-circuit potential, a result is obtained which is different from that shown in Fig. 3. Figure 4 shows the plots of E_{corr}, C, and R vs. the immersion time in 3% NaCl for Specimen A which is held at a potential of −0.5 V. It is found that with increasing time E_{corr} steadily decreases whereas C steadily increases. However, the polarization resistance R changes more pronouncedly with time compared with E_{corr} and C. The R abruptly drops in value once the pitting occurs. Thus the sharp change in the R value may be more suitably used when monitoring the onset of the pitting process. In view of the large changes in the R and C values during the pitting process, it is believed that the onset and the development of pitting can be monitored by an analysis of the R and C values obtained from the impedance spectra at a suitably fixed potential. In this case, it is suggested that the corrosion potential developed at the moment of sample immersion in the solution be chosen as the fixed potential.

The AC impedance spectra at the open-circuit potential for Specimen B during immersion in 3% NaCl solution at various times show that the R value decreases with an increasing time of immersion. This is because Specimen B has a better pitting-corrosion resistance than Specimen A. In comparison with Specimen A, Specimen B has a much larger R as well as a more positive E_{corr}. Figure 5 shows the plots of C and R vs. the immersion time in 3% NaCl solution for Specimen B at the open-circuit potential. The resistance R shows a large initial decrease and then it becomes steady. On the other hand, C shows a relatively large initial increase and then levels off after. Therefore, for samples with a better pitting-corrosion resistance, the detection of the onset of the pitting process can be carried out at open-circuit potentials with the AC impedance spectroscopy.

Conclusions

From our experimental observations, the following conclusions can be made.

1. When impedance measurements are carried out at the open-circuit potentials, it is found at the earlier stage of pitting that with increasing immersion time, R increases for poorer pitting-corrosion resistant materials and decreases for better pitting-corrosion resistant materials.

2. AC impedance spectroscopy at the corrosion potential E_{corr} can be used to evaluate pitting-corrosion resistance of high-chromium cast iron. After immersion in solution for a certain period of time, the presence of a larger polarization resistance R and a smaller capacitance C indicate a better pitting-corrosion resistance of the material.

3. AC impedance spectroscopy at a fixed potential, the fixed potential being chosen as the corrosion potential E_{corr} developed at the moment when the sample is immersed in solution, can be used to detect the onset of the pitting process. For the electrode on which pitting occurs, the R value abruptly drops at the initial stage of pitting, whereas for the electrode on which pitting does not occur, R remains unchanged or even increases.

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