Research Article

Improve thement of Pitting Corrosion Resistance of Type 316L Stainless Steel by Potentiostatic Removal of Surface MnS Inclusions

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The beneficial effect of the removal of MnS inclusions on the pitting of stainless steels has been demonstrated in two ways. (1) High-purity Type 316L stainless steel with no inclusions was used as a specimen in the measurement of anodic polarization curves in 0.5 M NaCl and (2) commercial Type 316L stainless steel with MnS and slag-related inclusions was first polarized at different potentials for 30 min in 1 M Na2SO4 of pH 3 and then anodic polarization measurements were taken in 0.5 M NaCl. Pitting did not occur in the passive or transpassive region of the high-purity steel. The polarization treatment dissolved MnS and some oxide inclusions (CaO and SiO2) on the surface of the commercial steel. An increase in pitting potential of the commercial steel was noted after treatment at potentials above 0.2 V. At the same time, the number of current spikes due to metastable pits decreased significantly. These results are more likely due to the beneficial effect of removing MnS inclusions from the steel surface rather than the modification effect of the chemical composition of passive films on the surface.

1. Introduction

Manganese sulfide (MnS) inclusions are known to act as the initiation sites of pitting corrosion on stainless steels [1–9], while the overall dissolution of the inclusions is not necessary for the formation of pit initiation sites [10–17]. It is therefore expected that the removal of surface MnS inclusions improves the pitting corrosion resistance of stainless steels. The aim of treating the surface of stainless steels with processes like nitric acid passivation (ASTM A380 and ASTM A967) is to form a stable Cr-enriched passive oxide film [18], which plays an important role in providing high corrosion resistance to stainless steels. Such surface treatment has an additional effect of dissolving and removing the MnS inclusions from the surface of stainless steels [19]. Therefore, the improvement of pitting corrosion resistance by passivation treatments can be attributed not only to the modification of the chemical composition of the passive films but also to the removal of MnS from the surface of stainless steels. However, these two effects cannot be distinguished from each other in practice. For the further development of passivation treatments of stainless steels which meet environmental regulations and human safety standards, it is important to understand the intrinsic mechanism of each effect provided by passivation treatments.

The purpose of the present study is to examine solely the effect of removing MnS on the pitting corrosion resistance of austenitic stainless steels. To realize this purpose, surface MnS inclusions were removed by potentiostatic anodic polarization in a weakly acidic Na2SO4 solution and the pitting corrosion resistance was then examined by potentiodynamic polarization in a neutral NaCl solution.
2. Experimental

Commercial Type 316L and high-purity Type 316L stainless steels were used as specimens. The chemical composition of the steels is given in Table 1. The high-purity Type 316L steel was prepared by a vacuum induction melting method using electrolytic Fe, Cr, and Ni and high-purity Mo as starting materials. Plates with dimensions of $15 \times 25 \times 2$ mm were cut from cold rolled sheets and heat-treated at $1323 \, \text{K}$ for 0.5 h followed by water quenching. The specimens were mechanically ground with SiC paper through a 1500 grid and cleaned ultrasonically with acetone. The specimen surfaces, except for the electrode area of $10 \times 10$ mm, were covered with epoxy resin and subsequently with paraffin.

To evaluate the pitting corrosion resistance, potentiodynamic polarization measurements were carried out with a conventional three-electrode cell. The electrolyte solution was 0.5 M NaCl at 298 K. The solution was deaerated with purified N$_2$ for more than 30 min before the measurements. The potential scan rate was $3.8 \times 10^{-4} \, \text{V s}^{-1}$ ($23 \, \text{mV min}^{-1}$). The polarization was started from 50 mV lower than the open-circuit potential after immersion in the test solution for 10 min. The reference electrode was an Ag/AgCl (3.33 M KCl) electrode. All the potentials cited in this paper refer to this electrode.

In order to remove MnS inclusions from the surface of specimens, potentiostatic polarization treatment was performed at different potentials of 0.1 to 0.5 V for 30 min in 1 M Na$_2$SO$_4$ of pH 3. The solution pH was adjusted with the addition of a small amount of 1 M H$_2$SO$_4$. Immediately after potentiostatic polarization treatment, the potentiodynamic anodic polarization curves in 0.5 M NaCl were measured in the manner described above.

A JEOL JSM-6510 scanning electron microscope (SEM) equipped with a JEOL JED-2300 energy dispersive X-ray spectrometer (EDS) was employed to analyze the inclusions on the surface of the specimens. The accelerating voltage was set at 20 kV. The specimens used for the SEM/EDS analysis were first mirror polished with a diamond paste of 1 $\mu$m.

### Table 1: Chemical composition of specimens (wt%).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial type 316L</td>
<td>0.022</td>
<td>0.69</td>
<td>0.9</td>
<td>0.027</td>
<td>0.004</td>
<td>12.08</td>
<td>17.25</td>
<td>2.09</td>
<td>—</td>
</tr>
<tr>
<td>High-purity type 316L</td>
<td>0.004</td>
<td>0.01</td>
<td>0.01</td>
<td>0.003</td>
<td>0.001</td>
<td>14.78</td>
<td>17.4</td>
<td>2.63</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Figure 1 shows the anodic polarization curves of as-polished commercial Type 316L and high-purity Type 316L stainless steels in 0.5 M NaCl. The commercial steel exhibits many current spikes in the potential range from 0.2 V to 0.6 V and a sharp increase in current at around 0.6 V. These two characteristic events can be attributed to the formation of metastable pits and the growth of a stable pit, respectively. In the polarization curve of the high-purity steel, no characteristic pitting event was observed in the passivity and transpassivity region from 0.0 V to 1.2 V. No pit initiation sites were found on the surface of the high-purity steel.

Round inclusions with a diameter of 5 to 10 $\mu$m were observed on the surface of as-polished commercial Type 316L stainless steel. Figure 2 shows the SEM image and EDS elemental maps of a typical inclusion in the commercial steel. A skin of steel partly covers the central part of the inclusion. The inclusion consists mainly of oxides, CaO, SiO$_2$, Al$_2$O$_3$, and MgO, which come from steel making slag. Small MnS particles are distributed in the peripheral region of the oxide inclusion. Because a skin of steel partly covers the inclusion, MnS particles observed in the central part of the inclusion are actually not inside but outside the oxide inclusion. The dissolution of MnS at the boundary region between the inclusion and the steel matrix is thought to have triggered the pitting observed in Figure 1. No visible inclusion was detected on the surface of the high-purity steel.

The results of the previous study using a microelectrochemical technique suggest that MnS inclusions undergo electrochemical dissolution under anodic polarization in neutral solutions [10–17]. Figure 3 shows the SEM image and EDS elementary maps of commercial Type 316L stainless steel after potentiostatic polarization at 0.5 V for 30 min in 1 M Na$_2$SO$_4$ with pH 3. This SEM/EDS analysis was performed in the same region as the images in Figure 2. Not only MnS but also CaO and SiO$_2$ components were dissolved by the polarization treatment. Spinel (MgAl$_2$O$_4$) and perovskite (CaTiO$_3$) remained undissolved after polarization treatment. According to the potential-pH diagram of MnS-H$_2$O system [20], the stable Mn and S species in the potential range of 0.1 V to 0.5 V at pH 3 were Mn$^{2+}$ and S$_2$O$_3^{2-}$ ions, respectively. Therefore, MnS undergoes
the following oxidative dissolution during the polarization treatments:

$$2\text{MnS} + 3\text{H}_2\text{O} \rightarrow 2\text{Mn}^{2+} + \text{S}_2\text{O}_3^{2-} + 6\text{H}^+ + 8e^- \quad (1)$$

The dissolution of CaO and SiO$_2$ is caused by chemical reactions. Since SiO$_2$ itself is insoluble in weakly acidic solutions, the disappearance of SiO$_2$ after the treatments reveals that SiO$_2$ forms soluble calcium silicate such as 2CaO•SiO$_2$ and 3CaO•SiO$_2$ in the inclusion.

The effect of potentiostatic polarization treatments on the pitting corrosion resistance of commercial 316L stainless steel was examined by measuring the anodic polarization curves in 0.5 M NaCl. Figure 4 exhibits three anodic polarization curves after the same polarization treatment at 0.5 V for 30 min in 1 M Na$_2$SO$_4$. Compared with the as-polished specimen shown in Figure 1, fewer current spikes due to metastable pitting were noted and the onset potential of stable pitting was higher. However, the characteristics of the parameters of pitting varied from experiment to experiment, as can be seen in Figure 4. This indicates that the pitting had a randomness or a probabilistic property [21–23]. In order to statistically treat the pitting properties, we repeated the anodic polarization measurement at least eight times for each treatment condition. The following three electrochemical parameters were evaluated from each of the polarization curves: the onset potential of metastable pitting, $E_r$, the onset potential of stable pitting, $E_{pit}$, and the number of metastable pits, $N_{msp}$, which is assumed to be equal to the number of
current spikes in the potential region between $E_r$ and $E_{pit}$. The distribution of each of these parameters was examined using a normal probability paper.

Figures 5, 6 and 7 show the normal probability plots of the distribution of $E_r$, $E_{pit}$, and $N_{mp}$, respectively. Linear relationships were observed for the three parameters examined, suggesting that the scattering of data follows a normal distribution. The average value of $E_r$, which is the value of $E_r$ at the cumulative probability of 50%, increased gradually with increasing treatment potential, while the slope of the normal probability plot, which corresponds to the reciprocal of standard deviation, remained unchanged. The average value of $E_{pit}$ increased significantly with increasing treatment potential and, at the same time, the slope of the normal probability plot became less steep. The latter result is due to the fact that very high $E_{pit}$ values above 1.0 V were obtained for several specimens treated at potentials higher than 0.2 V. In other words, the scattering of $E_{pit}$ data originates not only from the intrinsic nature of the pitting process but also from the variation of the effectiveness of polarization treatments for eliminating pit initiation sites.

In Figure 7 the average value of $N_{mp}$ decreases remarkably with polarization treatment. The average value of $N_{mp}$ for specimens treated at potentials above 0.3 V is at least one order of magnitude lower than that for the as-polished specimen, indicating that the number of pit initiation sites decreased significantly with the polarization treatments employed in this study. The decrease in the number of pit initiation sites may well explain the observed increase in $E_{pit}$. However, there is also a possibility that the passivation effect, that is, the Cr enrichment in passive films, was induced by the polarization treatment and that this led to the improvement of pitting resistance.

To examine the passivation effect, the anodic polarization curves in 0.5 M NaCl were measured after the following nitric passivation treatment: the immersion of specimens in 30% HNO$_3$ at 60°C for 1 h. A typical result is shown in Figure 8 and compared with another result after the polarization treatment at 0.5 V. After the nitric acid passivation treatment, no metastable pitting was observed and stable pitting occurred only at a very high potential of about 1.1 V (see also Figure 6). Even though the pitting potential of the two specimens shown in Figure 8 is almost identical, the current densities in the passivity and transpassivity regions are quite different. The current density of the specimen passivated in nitric acid was extremely low in the passivity region but increased remarkably with potential in the transpassivity region above 0.6 V. Such a large change in the current density...
of the specimen passivated in nitric acid can be explained by the presence of a passive film enriched with Cr oxide. The presence of Cr oxide suppresses dissolution in the passive state but accelerates dissolution in the transpassive state to form soluble Cr (VI) species.

The passive current density at 0.3 V, \( i_{\text{pass}} \), in 0.5 M NaCl was read from all the polarization curves measured, and its average value was calculated and then plotted against the polarization treatment potential in Figure 9. While the average value of \( i_{\text{pass}} \) decreased slightly with increasing treatment potential, it was always one order of magnitude higher than that for specimens passivated in nitric acid and was rather close to that for as-polished specimens. It is therefore suggested that the polarization treatment used in this study did not have a strong passivation effect but had the significant beneficial effect of reducing the number of pit initiation sites.

4. Conclusions

By comparing the anodic polarization curves in 0.5 M NaCl for high-purity Type 316L stainless steels with those of commercial 316L stainless steels, it is confirmed that the removal of MnS is essential to derive excellent pitting corrosion resistance. Manganese sulfide (MnS) and some oxide (CaO, SiO2) inclusions on the surface of commercial Type 316L stainless steels were dissolved by potentiostatic polarization treatments in 1 M Na2SO4 with pH 3. After polarization treatment, the number of current spikes due to metastable pitting decreased significantly and the pitting potential increased, while the passive current density did not change as remarkably as for specimens subjected to nitric passivation treatment. The elimination of pit initiation sites rather than the modification of the chemical composition of passive films is important to improve the pitting corrosion resistance of stainless steels.

References


