Surface white spot and pitting corrosion of 316 L stainless steel

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Abstract
Purpose – The purpose of this paper is to address the concern of some stainless steel users. To understand the effect of surface white spots on corrosion performance of stainless steel.

Design/methodology/approach – White spots appeared on some component surfaces made of 316 L stainless steel in some industrial applications. To address the concern about the pitting performance in the spot areas, the pitting corrosion potential and corrosion resistance were measured in the spot and non-spot areas by means of potentiodynamic polarization and electrochemical impedance spectroscopy and the two different surface characteristics were analytically compared by using optical microscopy, laser confocal microscopy, scanning electron microscopy, x-ray diffraction, energy dispersive spectroscopy and auger energy spectroscopy. The results indicated that the pitting performance of the 316 L stainless steel was not negatively influenced by the spots and the white spots simply resulted from the slightly different surface morphology in the spot areas.

Findings – The white spots are actually the slightly rougher surface areas with some carbon-containing species. They do not reduce the pitting resistance. Interestingly, the white spot areas even have slightly improved general corrosion resistance.

Research limitations/implications – Not all surface contamination or roughening can adversely affect the corrosion resistance of stainless steel.

Practical implications – Stainless steel components with such surface white spots are still qualified products in terms of corrosion performance.

Originality/value – The surface spot of stainless steel was systematically investigated for the first time for its effect on corrosion resistance and the conclusion was new to the common knowledge.

Keywords Pitting, Stainless steels, Passivity, Surface

Paper type Technical paper

1. Introduction

Stainless steels have good mechanical properties and excellent general corrosion performance because a protective passive oxide film can be naturally formed on their surface, and thus they have various applications (You et al., 2007; Yang and Ren, 2010; Talha et al., 2013). Nevertheless, pitting corrosion is always a big issue of the metallic materials, as it may lead to unexpected failures of structures.

Many researchers have studied various environmental influences on the passivity or pitting behavior of stainless steels such as anions, medium pH and strain (Pistorius and Burstein, 1994; Hong and Nagumo, 1997; Zuo et al., 2002; Lü et al., 2008; Li et al., 2014). For example, Zuo et al. investigated the effect of anions $PO_4^{3-}$, $CrO_4^{2-}$, $SO_4^{2-}$ and $NO_3^{-}$ on the metastable pitting performance of 316 L stainless steel in NaCl solutions and concluded that these anions could decrease the solution acidity, and thus improve the steel passivity, the metastable pitting could be suppressed by these anions in the order of $PO_4^{3-} > CrO_4^{2-} > SO_4^{2-} > NO_3^{-}$ due to their different hydrolysis levels (Zuo et al., 2002). However, it was also found that the electrolyte pH had no prominent effect on the metastable pitting initiation for AISI 304 stainless steel because the pH inside the corroding pit was determined by the hydrolysis of the soluble corrosion products and the dissolution current density (Pistorius and Burstein, 1994).

In fact, the passivity and pitting of stainless steel are more fundamentally determined by the steel itself, i.e. the steel microstructure and composition (Pardo et al., 2008; Jung et al., 2018). A large number of publications have been focused on the effects of alloying elements and the mechanisms of passivation and pitting behaviors (Song et al., 1994; Olsson and Landolt, 2003; Song, 2005; Song et al., 2005). These factors also include metallurgical parameters such as heat-treatment conditions and post-treatment (Laleh et al., 2020; Sugawara et al., 2018; Muller et al., 2015; Edwards et al., 2016). For instance, it has been found that high-temperature post-treatment can lead to the formation of deleterious MnS inclusions, and thus result in an unanticipated drastic decline in the pitting resistance of selective laser melting (SLM) produced 316 L stainless steel (Laleh et al., 2020). AISI 304 stainless steel after plasma carburizing in $H_2$-$CH_4$ atmosphere and subsequent post-pickling treatment in an HF-$HNO_3$ solution does not exhibit pitting damage under the anodic polarization even in a 3 M NaCl solution, because the pickling treatment can remove the Cr-depleted zones formed during the plasma carburizing (Sugawara et al., 2018).
Both the environmental and the metallurgical factors can affect the passivity and pitting performance of stainless steel through influencing its surface state that directly determines the integrity, protectiveness and stability of the passive film on the surface (Choi et al., 2013; Klapper et al., 2013; Kim et al., 2017; Liu et al., 2012; Hannani and Kermiche, 1998). The surface can be modified by various processes such as ion implantation and pickling. Klapper et al. demonstrated that the pickled surfaces of stainless steels were less stable and more susceptible to pitting corrosion when they were passivated in a low-humidity environment (Klapper et al., 2013). However, nitrogen ion implantation was reported to improve the stability of passive films and the pitting resistance of austenitic steel AISI 304 (Hannani and Kermiche, 1998). These treatments modified the surface state or the passive film of the stainless steels, and thus influenced the pitting resistance and passivity.

It is important to understand the effects of detailed surface state parameters on the pitting corrosion of the stainless steel, as the surface treatments like acid pickling can influence the pitting behavior of stainless steel (Choi et al., 2013; Klapper et al., 2013; Rockel and Herda, 1992). Such research closely concerns the optimization of production processes/procedures for stainless steel components. Compared with those investigations into the effect of metallurgical and environmental factors on passivity and pitting corrosion, there are relatively few studies on some practical problems such as surface cleanliness, during stainless steel production and product/component fabrication, particularly the potential influence of these practical issues on the final pitting resistance. For example, some white spots were observed on the autogenous Tungsten Inert Gas welds of a cryogenic Fe-36% Ni steels, which were detected to be oxides containing the minor elements Ca, Al, Mg of the steels (Lee, 2019). However, no further study has been carried out to investigate the possible influence of these white spots on the pitting corrosion of the steels.

In exploring the surface state parameters critical to pitting, we recently interestingly found that some white spots appeared on the surface of 316L stainless steel after acid pickling. It would be of scientific curiousness and engineering necessity to look at the nature of these surface spots and their possible influence on pitting corrosion. To our best knowledge, currently, there were very few investigations on this topic.

2. Materials and methods

2.1 Material and specimen preparation

The stainless steel used in this work was commercially available cold-rolled 316L sheets, which were cut into 150 mm × 200 mm × 6 mm coupons. The chemical composition of the 316L stainless steel is listed in Table 1. After pickling in a mixed acidic solution containing 120~150 g/L HNO3 and 30 g/L HF at 45 ~ 50°C for about 3 min in TAIYUAN IRON & STEEL (GROUP) CORPORATION, some white spots could be visualized on the steel, and thus appeared on the cut coupons. All the coupons were successively rinsed by acetone, ethyl alcohol and deionized water for the following experiments. The white spots were not affected by the rinse process at all.

2.2 Electrolyte cell setup

The existence of crevice corrosion can strongly distort the measurement of pitting corrosion (Galvele, 2005). To avoid crevice corrosion and to ensure the accuracy of the pitting potential measurement, a double-model cell (DMC) device in this work was used in this study (Shen et al., 2019). The critical parts of the DMC are schematically illustrated in Figure 1. A platinum counter electrode and a KCl-saturated Ag/AgCl reference electrode with a fixed potential of +0.2224 V relative to the standard hydrogen electrode were embedded in the syringe tube. The syringe “mouth” was above the sample surface and the distance d from the coupon surface to the “mouth” could be adjusted to avoid crevice corrosion during the electrochemical measurements in this study. The diameter of the syringe “mouth” was around 9.4 mm and the contacting surface area of the sample exposed to the test solution was 0.69 cm².

2.3 Electrochemical measurements

Potentiodynamic polarization experiments were carried out in spot areas and non-spot areas with the DMC at room temperature. A 3.5 wt.% NaCl solution (pH ~ 6.8) was used as the corrosive electrolyte. A cathodic polarization potential −0.8 V was first applied to the electrode for 10 min using an electrochemical workstation (IVIUM-43228, Holland) to further clean the sample surface, then it was left at its open circuit potential measurement, a double-model cell (DMC) device in this study (Shen et al., 2019). The critical parts of the DMC are schematically illustrated in Figure 1.

Table 1. Chemical composition of stainless steel 316L

<table>
<thead>
<tr>
<th>Element</th>
<th>S</th>
<th>C</th>
<th>P</th>
<th>N</th>
<th>Cu</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>0.001</td>
<td>0.021</td>
<td>0.028</td>
<td>0.052</td>
<td>0.054</td>
<td>0.500</td>
<td>1.167</td>
<td>2.11</td>
<td>10.132</td>
<td>17.343</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
circuit potential (OCP) for 10 min to reach its steady-state. After that, potentiodynamic polarization was performed at a scan rate of 0.167 mV/s from −0.8 V to 0.9 V vs the saturated Ag/AgCl electrode. The pitting potential was recorded when the current density jumped up to 10 µA/cm². All the potentials mentioned in this paper were relative to the KCl-saturated Ag/AgCl electrode.

Electrochemical impedance spectroscopy (EIS) was also performed in the DMC containing 3.5 wt.% NaCl using the same electrochemical workstation from 17.8 kHz to 10 mHz with an AC potential amplitude of 5 mV after the specimen was stabilized at its OCP for 30 min.

The potentiodynamic polarization and EIS measurements were repeatedly conducted on 20 different white spot areas and 20 non-spot areas, respectively. Their values were statistically analyzed.

2.4 Surface characterization
The surface morphology of the samples was characterized using an optical microscope (LEICA DVM6a, Germany). A table scanning electron microscope (SEM, Phenom-World Phenom XL, Holland) under the secondary electron mode was used to further reveal the surface details. The surface roughness was measured using a laser confocal microscope (LSM, Keyence VK-X200K, Japan). To guarantee the reliability of the roughness measurement, four parallel samples were used and on each sample, the measurement was executed 20 times in an area of 100 × 100 µm².

2.5 Phase and element analyzes
X-ray diffraction (XRD, Bruker-axs, USA) was used to analyze the phases in the surface layer. The XRD used a copper target with 2.2 kW power at 40 kV and 40 mA, scanning from 20° to 90° at 0.1°/step. The spectral analysis and phase identification were carried out using Jade 6.5 software. The elements in the sample surface were analyzed by Energy Dispersive X-Ray spectrometry (EDS, Phenom-World Phenom XL, Holland) and Auger Electron Spectroscopy (AES, Physical electronics PHI660, USA).

3. Results
3.1 Pitting potential
The typical potentiodynamic polarization curves of the 316 L in the spot and non-spot areas are shown in Figure 2. The two polarization curves appeared to be quite similar. They had an abrupt rise in current density after passivation at similar potentials, which corresponding to their slightly different pitting potentials; the spot area was slightly higher than the non-spot area in pitting potential.

The above similarity or the slight difference was further confirmed after their repeated measurements in a different spot and non-spot areas. The measured pitting potentials had statistically a normal or Gaussian distribution (Figure 3). Although the data points had a wide scattering range, the large number of repeated measurements could significantly narrow the standard deviation. The fitted results as shown in Figures 3(a) and 3(b) indicated that the mean (µ) ± standard deviation (σ) of the pitting potentials of the non-spot areas and spot surface areas were 0.552 ± 0.129 V and 0.572 ± 0.124 V, respectively. The

Figure 2 Typical polarization curves of the 316 L in spot and non-spot areas in 3.5 wt.% NaCl solution

Figure 3 Statistic distributions and Gaussian fitting curves for pitting potentials

Notes: (a) Non-spot area; (b) spot area repeatedly measured on parallel areas in pitting potential

spot areas were on average only 20 mV higher than the non-spot areas in pitting potential.

3.2 Electrochemical impedance spectroscopy results
EIS measurements were conducted to assess the resistance of the passive film formed after the acid pickling. The typical Bode spectra gained from the spot and non-spot areas are shown in Figure 4. The impedance in the high-frequency range from 10³ to 10⁵ Hz could be related to the electrolyte resistance (Chang and Park, 2010; Revilla et al., 2020). A distinct capacitive behavior observed in the frequency range from 10⁻² to 10⁵ Hz could be a result of the passive film on the 316 L surface. The phase angle plots suggested that only one time-constant was
involved in the system, which could be associated with the dissolution and formation of the passive film and the non-Paradise charging across the film. The statistic values of the impedance repeatedly measured in the spot and non-spot surface areas at the low frequency $10^{-2}$ Hz are presented in Figure 5, indicating that the spot area was slightly more resistant than the non-spot area. This slight difference in low-frequency impedance was in agreement with what was expected from the polarization curves earlier.

The Bode spectra presented in Figure 4 if converted into Nyquist plots will be incomplete capacitive loops with only the imaginary curves nearly vertical to the real axis. Several equivalent electrical circuits (EEC) have been proposed in the literature to estimate the passive film capacitance from the measured EIS data (Kerrec et al., 1995; Woldemedhin et al., 2012; Orazem et al., 2013; Liu et al., 2014; Evertsson et al., 2015; Revilla et al., 2020). For simplicity, a simple Randle circuit (Figure 6) containing a solution resistance ($R_s$) in series connected with a combination of a passive film resistance ($R_\varphi$) parallel with a passive film capacitance ($C$) which can be represented by a constant phase element (CPE) due to the non-ideal surface of the passive film was used to fit the EIS spectra of the spot and non-spot areas. A measured CPE can be converted into $C$ (Hsu and Mansfeld, 2001) according to:

$$C = Y_0(\omega_{\text{max}})^{n-1}$$

where $\omega_{\text{max}}$ is the angular frequency at which the imaginary part of the impedance ($-Z_\imath$) reaches its maximum value in the Nyquist plot, $Y_0$ is a constant obtained by curve fitting from the measured EIS and the fitted $n$ ranging from 0.5 to 1 represents the ideality of the film surface. The average values and standard deviations of the fitted equivalent circuit parameters are shown in Table 2. The differences between the spot and non-spot areas were very small, the passive film resistance in the spot area only very slightly higher than that of the non-spot area and the film capacitance of the former was slightly lower than that of the latter. The values of $n$ are close to 1, suggesting the passive films formed in these two different areas were nearly perfect.

The EIS results (Table 2) further suggest that the spot area might have slightly higher general corrosion resistance than the non-spot area in non-polarized immersion conditions. The slightly higher passive film resistance and lower passive film capacitance could result from a slightly thicker film formed in the spot area. Certainly, the $R_\varphi$ and $C$ measured at the OCP cannot be directly related to the pitting corrosion resistance under anodic polarization, they provide some information about the film formed under natural immersion. This film may evolve with increasing potential and indirectly influence the pitting potential.

### 3.3 Surface morphology

Figure 7 showed the optical images of a typical region with white spot and non-spot areas before and after pitting corrosion. The spots were visible by the naked eye [Figure 7(a)] and could be better distinguished under a microscope [Figure 7(b)]. The non-spot area [Figure 7(c)] was very uniform. The pitting corrosion morphology in the spot area [Figure 7(d)] was similar to that in the non-spot area [Figure 7(e)].

SEM further revealed the surface characteristics of the spot and non-spot areas in more detail before pitting (Figure 8). Figure 8(a) shows a boundary between the non-spot area and spot area. The magnified images indicated that the spot area was rougher than the non-spot area [Figures 8(b) and 8(c)].

### 3.4 Surface roughness

To confirm the difference in surface roughness indicated by the SEM observation (Figure 8), the LSM was used. The roughness readings presented in Figure 9(a) clearly suggested that the spot area was rougher than that of the non-spot area, which was consistent with the surface morphology results in Figures 8(b) and 8(c). The surface profile analysis is shown in Figure 9(b) also proved the higher roughness of the spot area than the non-spot area.

### 3.5 Surface microstructure

The XRD results of the spot and non-spot areas are shown in Figure 10. These two areas had exactly the same diffraction peaks corresponding to (111), (200) and (220) crystal planes, respectively, which indicated that the difference between them in microstructure was insignificant. It is actually understandable if the white spot was a very surficial phenomenon and did not have a different microstructure in the depth detectable by XRD.

### 3.6 Surface composition

Figure 11 shows the EDS mapping results of the 316L surface containing spot and non-spot areas. The surface [Figure 11(b)] had elements Fe, C, Cr, Mn, Mo and Si and their distributions [Figures 11(c) and 11(d)] were quite uniform over the whole surface. Much more carbon dots appeared in the spot area than in the non-spot area. Again, as EDS detection depth is a few micrometers, the differences between the spot and non-spot areas may be too surficial to detect and if any could be overwhelmed by the background signals.
To detect the possible surficial differences, AES analysis was implemented. Figure 12 shows the AES results acquired from the non-spot area [Figure 12(a)] and spot area [Figure 12(b)]. It appeared that the C content in the spot area (46.4 wt.%) was higher than that in the non-spot area (18.7 wt.%), while the O and Fe contents were lower.

### 4. Discussion

The measured pitting potentials (Figure 3) showed that the spot area had even a slightly higher pitting potential than the non-spot area, suggesting that the appearance of white spots on the surface at least did not deteriorate the pitting performance of a component made of 316L stainless steel. The EIS results (Figures 4 and 5 and Table 2) provided a preliminary interpretation for the higher pitting resistance in the spot area; the passive film resistance $R_p$ in the spot area was slightly higher than that in the non-spot area, meaning that the film in white spot area could be thicker or more compact in some senses than that in the non-spot area.

<table>
<thead>
<tr>
<th>Test area</th>
<th>$R_0$(Ω)</th>
<th>$Y_0$(Z$^{-1}$)</th>
<th>$n$</th>
<th>$R_p$(Ω)</th>
<th>C(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot area</td>
<td>44.8</td>
<td>$2.38 \times 10^{-25}$</td>
<td>0.916</td>
<td>$3.39 \times 10^{-06}$</td>
<td>$3.06 \times 10^{-05}$</td>
</tr>
<tr>
<td>±3.37</td>
<td>±1.79 $\times 10^{-25}$</td>
<td>±0.018</td>
<td>±2.20 $\times 10^{-06}$</td>
<td>±2.46 $\times 10^{-05}$</td>
<td></td>
</tr>
<tr>
<td>Non-spot area</td>
<td>51.6</td>
<td>$2.59 \times 10^{-25}$</td>
<td>0.909</td>
<td>$3.27 \times 10^{-06}$</td>
<td>$3.40 \times 10^{-05}$</td>
</tr>
<tr>
<td>±15.9</td>
<td>±1.90 $\times 10^{-25}$</td>
<td>±0.019</td>
<td>±2.89 $\times 10^{-06}$</td>
<td>±2.66 $\times 10^{-05}$</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 7** Optical images of spot area and non-spot areas on 316 L stainless steel surface before and after pitting corrosion

**Notes:** (a) A surface region with white spots; (b) a white spot area; (c) a non-spot area; (d) pitting in a spot area; (e) pitting in a non-spot area

To detect the possible surficial differences, AES analysis was implemented. Figure 12 shows the AES results acquired from the non-spot area [Figure 12(a)] and spot area [Figure 12(b)]. It appeared that the C content in the spot area (46.4 wt.%) was higher than that in the non-spot area (18.7 wt.%), while the O and Fe contents were lower.

**Figure 8** SEM images of the 316 L stainless steel surface

**Notes:** (a) A region with spot and non-spot areas; (b) the enlarged non-spot area; (c) the enlarged spot area

**Figure 9** 316L stainless steel LSM results

**Notes:** (a) Surface roughness; (b) surface profile

The optical images (Figure 7) indicated that the spot area was more heterogeneous in morphology, and the SEM images (Figure 8) confirmed the spot area rougher than the non-spot area. The roughness $R_a$ measurements over the spot and non-spot areas quantitatively demonstrated the difference of surface roughness was significant, around 0.4 μm (Figure 9). There have been several publications on the influence of surface roughness on pitting corrosion of stainless steels (Tang et al., 2019; Lee et al., 2012; Moayed et al., 2003; Hong and Nagumo, 1997; Sasaki and Burstein, 1996). Although some of them have proved that a smoother surface has improved pitting corrosion resistance, the corrosion resistance of stainless steel has also been reported to be poorly correlated with the surface roughness when
Ra is greater than 0.5 \( \mu m \) (Lee et al., 2012). This was probably because a further increase in roughness could only change the morphologic geometry, but could not effectively increase the number or the size of the surface defects. In this study, the surface roughness results of the spot and non-spot areas were both larger than 0.5 \( \mu m \). In this case, the roughness difference would not impact pitting performance significantly anymore.

The capacitance results obtained from the fitted EIS spectra suggested that the spot area might have a thicker passive film than the non-spot area, as an increase in thickness can lead to a smaller capacitance. The higher film resistance had supported that the spot area is likely to have a thick film. This is could be an important reason for the slightly higher pitting resistance in the spot area. It appears that an increase in film thickness could more significantly affect the capacitance and the pitting resistance than a change in film roughness. To interpret this, other factors associated with the film thickness should also be considered.

The similar XRD results between the spot and non-spot areas (Figure 10) experimentally excluded the possibility of the phase difference is responsible for their slight difference in pitting corrosion resistance. Another difference between the spot and non-spot areas was the carbon content (Figures 11 and 12). The contaminants might originate from the detergent used in rinsing or some pollutants in production procedures. If a very thin adsorptive organic film was adsorbed or deposited in the spot area, it might slightly roughen the surface, but still, decrease the surface capacitance, increase the corrosion resistance or pitting potential.

The white spots on the 316 L surface were visible, particularly under an optical microscope. This was likely due to its rougher surface. The contamination if any might also be contributed to the difference in color.

Based on the discussion above, the different surface states of the spot area could not significantly lower the corrosion resistance of 316 L stainless steel. Hence, the appearance of some white spots on a component made of 316 L stainless steel surface will not have reduced pitting corrosion resistance. With regard to the mechanism of the spot formation, more research work is needed, which has been planned in a follow-up study.

5. Conclusions

Based on the electrochemical results and surface analyzes, the following conclusions can be drawn:

- The pitting performance of 316L stainless steel in a white spot surface area is not lower than in a non-spot area; and
- The white spot area is rougher than the other area and may be contaminated by some organic species.

References


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