Effect of low-temperature surface carburization on stress corrosion cracking of AISI 304 austenitic stainless steel

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A B S T R A C T

The effect of low-temperature surface carburization on the stress corrosion cracking (SCC) behavior of AISI 304 austenitic stainless steel in boiling magnesium chloride (MgCl2) solution at 155 ± 1 °C was investigated. The SCC tests were carried out for untreated and carburized AISI 304 with varying four-point bend loading. In order to elucidate the influence of low-temperature surface carburization on SCC resistance, optical microscope (OM), scanning electron microscope (SEM), X-ray diffractometry (XRD) and residual stress analyzer were used. The results show that the tensile stress on the surface of untreated four-point bend loaded AISI 304 and the occurrence of pits during SCC tests had bad influence on the SCC resistance. The surface of carburized four-point bend loaded AISI 304 was in a state of compressive stress over the whole loading range due to the presence of carburization-induced huge compressive residual stress. The chloride-induced SCC resistance of AISI 304 can be obviously improved by low-temperature surface carburization due the carburization-induced compressive residual stress and the improved pitting corrosion resistance. The carburization-induced compressive residual stress was the dominant reason for the improvement of SCC resistance. No relaxation happened in carburization-induced compressive residual stress and the phase of the expanded austenite was stable during SCC tests. © 2017 Elsevier B.V. All rights reserved.

1. Introduction

Austenitic stainless steels (ASS) are very widely used for industrial applications due to their good integrated performance and corrosion resistance. However, their modest mechanical (low surface hardness and strength) and tribological (high friction and wear rate) properties compared to other steels reduce their performance and lifetime in many engineering fields. Meanwhile, they are highly susceptible to localized forms of corrosion like pitting and SCC, especially chloride-induced SCC, which can lead to catastrophic failure.

Surface modification is one of the most effective technologies which can improve surface hardness and wear resistance of various engineering materials. In recent years [1–6], a novel low-temperature (below 500 °C) surface carburization process has been demonstrated which can significantly improve the mechanical and tribological properties without compromising their good corrosion resistance of ASS. Furthermore, the resistance of pitting corrosion can even be improved in chloride-containing solutions [7,8]. It is well known that SCC is one of the most severe maintenance problems in marine, medical and nuclear industries and low-temperature surface hardened ASS has already been used in these fields [9–11]. However, few studies investigated the effect of low-temperature surface carburization on SCC of ASS [9]. It has been generally accepted that SCC occurs as a result of the interaction of three factors [12–15]: susceptible material, corrosive environment and tensile stress. Ghosh et al. [16] demonstrated that the tensile residual stress induced by industrial fabrication can increase SCC susceptibility of ASS. Zhou et al. [17] have investigated the effect of surface grinding on chloride-induced SCC of 304L. They found that the surface tensile residual stress is the main factor causing the initiation of micro-cracks on ground surface during exposure. The pits tended to initiate at micro-cracks, which can act as precursors to macroscopic crack development. Lu et al. [18] have investigated effects of laser peening on SCC of 304 ASS. They found that the SCC resistance can be improved due to the generation of high level compressive residual stress and grain refinement during laser peening process. Therefore, the residual stress present in the material plays a key role in determining its SCC susceptibility in addition to the external stress working on the components in service. In fact, low-temperature surface carburization can generate very large compressive residual stress in the carburized layer of ASS [19,20]. However, the carburized layer is too shallow (few tens of microns), furthermore, the carburized layer consists of the austenite with the supersaturation of interstitial carbon atoms which is thermodynamically metastable [21,22]. All these factors may influence the SCC resistance of carburized ASS. Due to the effect of low-temperature surface carburization on SCC of ASS not yet being systematically investigated, therefore, there is a...
need to clarify the effect of low-temperature surface carburization on SCC of ASS.

The purpose of this paper was to investigate the effect of low-temperature surface carburization on chloride-induced SCC of AISI 304. Untreated and carburized AISI 304 were exposed in the test solution with varying four-point bend loading. The mechanism of low-temperature surface carburization on chloride-induced SCC of AISI 304 was revealed.

2. Material and experimental procedures

2.1. Material and low-temperature surface carburization

The material investigated in this work was the commercial type AISI 304 plate of 12 mm thickness in the solution-annealed state. The chemical composition of the steel was (in wt%): C 0.035, Si 0.436, Mn 1.10, P 0.031, S 0.0057, Ni 8.01, Cr 18.64, Mo 0.047, Cu 0.134, N 0.048 and Fe balance. The main measured mechanical properties of the steel along the rolling direction at room temperature are given in Table 1. For studying the effect of low-temperature surface carburization on chloride-induced SCC of AISI 304, two groups of the smooth strip specimens with dimensions of 69 × 15 × 3 mm³ were cut parallel to the rolling direction of the plate. The surfaces of all specimens were ground with emery papers down to No. 1200. Before stress corrosion tests, one group of the specimens was carburized at 470 °C for 30 h with a gas mixture containing CO, H₂ and N₂. The low-temperature surface carburization process used in this study was described in detail in previous work [23]. After carburization, the carburized specimens were lightly mechanically polished to remove the soot and the surface oxides that formed on cooling from the carburizing temperature.

2.2. Four-point bend loaded specimen preparation

Four-point bend loading was used to assess SCC susceptibility. The schematic diagram of the four-point bend loaded specimen is given in Fig. 1. In order to assess SCC susceptibility, the specimens were applied with different levels of maximum deflection (0.2, 0.35, 0.45 and 0.6 mm). According to ASTM G39 [24], the stress on the specimen surface under four-point bend loading can be calculated according to the following relationship:

\[ \sigma = \frac{12Ety}{(3H^2 - 4A^2)} \]

where \( \sigma \) = loading stress (surface stress for the mid-portion of the specimen), \( y \) = maximum deflection (between outer supports); \( E = 195 \) GPa, elastic modulus of AISI 304; \( t = 3 \) mm, the thickness of specimen; \( H = 60 \) mm, the distance between outer supports; \( A = 15 \) mm, the distance between inner and outer supports.

It should be noted that this relationship is valid only for stress below the elastic limit of the material according to the description of ASTM G39.

2.3. Stress corrosion tests

Before SCC tests, all specimens were cleaned by ultrasonic in ethanol in order to degrease the surfaces of the specimens. The SCC tests were performed in boiling MgCl₂ solution according to ASTM G36 [25]. The test solution was held at a constant boiling temperature 155 ± 1 °C with the help of a thermometer and water-cooled condenser. Periodic removal of the specimens from the solution was carried out to determine the crack initiation times. According to the recommendation of ASTM G36, all stressed surfaces should be examined at magnifications up to 20×. In this work, the cracks were detected by OM (AXIO Imager.A1m) at magnifications up to 25×.

2.4. Characterization of specimen

Surface morphologies and microstructures of cross-sections parallel to loading direction (after mechanically polishing with synthetic diamond grinding paste down to 3.5 μm and electrolytic etching in oxalic acid) of the specimens were investigated by SEM (Phenom ProX). The surface stresses parallel to the loading direction of the four-point bend loaded specimens were determined by PROTO-iXRD residual stress shows the apparatus used in the experiment, which was designed according to ASTM G36. The test solution was changed weekly in order to maintain the same concentration throughout the test period. Periodic removal of the specimens from the solution was carried out to determine the crack initiation times. According to the recommendation of ASTM G36, all stressed surfaces should be examined at magnifications up to 20×. In this work, the cracks were detected by OM (AXIO Imager.A1m) at magnifications up to 25×.

Table 1

<table>
<thead>
<tr>
<th>Mechanical properties of AISI 304.</th>
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<td>0.2% yield strength (MPa)</td>
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<td>282 ± 3</td>
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Fig. 1. Schematic diagram of the four-point bend loaded specimen.

Fig. 2. Assembled apparatus as per ASTM G36.
analyzer using the \( \sin^2 \Psi \) method with Mn-K\( \alpha \) X-ray (\( \lambda = 0.210314 \) nm). The reflection plane of the austenite was [311] and the diffraction angle was 144°. It should be noted that the stress determined using the XRD method is an arithmetic average value over the volume underneath the surface defined by the irradiated area (beam aperture with 1 mm diameter) and the effective information depth (6.9 \( \mu \)m for \( \Psi = 0^\circ \)) of the X-ray beam. The phase identification was determined by XRD (Rigaku SmartLab), performing \( \theta-2\theta \) scans from 30° to 90° with a scan speed of 10°/min using a Cu K\( \alpha \) X-ray (\( \lambda = 0.154056 \) nm) radiation source.

3. Results and discussion

3.1. Specimen characterization before SCC tests

3.1.1. Surface morphology and microstructure of specimen without external loading

The backscattered electron (BSE) images of SEM of the untreated and carburized surface morphologies are shown in Fig. 3. Although the surface of the carburized specimen was lightly mechanically polished, a little soot was still observed on the surface. In addition, there was hardly any difference in the surface morphologies between the untreated and carburized specimens under the SEM. Fig. 4 shows SEM images (BSE model) of the untreated and carburized surface microstructures, with obvious differences microstructures between the untreated and carburized specimens after electrolytic etching in oxalic acid. The microstructure of the untreated specimen showed the typical austenitic microstructure with some annealing twins. The carburized
The specimen showed typical signs of a deformation microstructure with extensive slip bands, similar to Gallo et al. [26] and Farrell et al. [27] who investigated the microstructural changes induced by low-temperature plasma carburization on ASS.

### 3.1.2. Surface stress under four-point bend loading

The surface stresses along the loading direction of the four-point bend loaded specimens are given in Fig. 5. The actual measured surface stresses deviated appreciably from the calculated values, especially for the carburized four-point bend loaded specimens. This is because of the residual stress and local plasticity. For the untreated four-point bend loaded specimens, the measured surface stresses were all in tensile state, although there was a $75 \pm 13$ MPa compressive residual stress in the surface layer prior to the loading (resulted from grinding operation). With the increasing loading levels, local plasticity of the specimen occurred and the measured values deviated increasingly from those calculated. For the carburized four-point bend loaded specimens, the measured surface stresses were highly compressive, and were attributed to the huge compressive residual stress ($-1586 \pm 73$ MPa) at the surfaces of the carburized specimens which were introduced during low-temperature surface carburization. It also should be noted that the curve of the measured surface stresses was linear over the whole loading range, which indicated that low-temperature surface carburization has significantly increased the local yield strength of the AISI 304.

### 3.2. Behavior of SCC

#### 3.2.1. Crack initiation time

The crack initiation time was defined in this work as when cracks first appeared and could be observed by OM at magnifications up to $25 \times$. The average crack initiation times for the four-point bend loaded specimens are given in Table 2. For the untreated four-point bend loaded specimens, all specimens cracked during SCC tests and the crack initiation times decreased with increasing loading levels, which indicated that the tensile stress had a negative effect on the SCC resistance. In contrast, no visible cracks were observed on the carburized four-point bend loaded specimens after SCC tests for a total of 720 h. These results clearly indicated that low-temperature surface carburization can significantly improve the chloride-induced SCC of ASS.

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**Fig. 6.** Surface morphologies of the four-point bend loaded specimens after SCC tests: (a) untreated specimen under 0.2 mm loading level, (b) untreated specimen under 0.6 mm loading level, (c) carburized specimen under 0.2 mm loading level, (d) carburized specimen under 0.6 mm loading level.

**Fig. 7.** Surface morphology of the carburized four-point bend loaded specimen under 0.6 mm loading level after a 24 h SCC test.
3.2.2. Surface morphology after SCC tests

The surface morphologies of the untreated and carburized four-point bend loaded specimens after SCC tests are shown in Fig. 6. All untreated four-point bend loaded specimens cracked during SCC tests and the cracks were all perpendicular to the loading direction. Pitting was observed in varying degrees for the untreated four-point bend loaded specimens and some of them followed the cracks, so that the cracks were sometimes seemed to extend from the pits, which indicated that pits may be precursors to the cracks. However, the results of SCC tests were very different for the carburized four-point bend loaded specimens. The surfaces were covered by a layer of corrosion products after 720 h SCC tests. It was hard to observe the surface morphologies under the corrosion products. Nevertheless, according to the morphologies of the cracks and pits on the surfaces of the untreated four-point bend loaded specimens, any cracks or pits on the surfaces of the carburized four-point bend loaded specimens can be easily identified if they existing. Thus, it was plausible that there were no cracks or pits on the

Fig. 8. Cross-section microstructures of the four-point bend loaded specimens after SCC tests: (a) untreated specimen under 0.2 mm loading level, (b) untreated specimen under 0.6 mm loading level, (c) carburized specimen under 0.2 mm loading level, (d) carburized specimen under 0.6 mm loading level.

Fig. 9. XRD patterns of the untreated and carburized four-point bend loaded specimens after SCC tests.

Fig. 10. Surface stress of the carburized four-point bend loaded specimen during SCC tests.
surfaces of the carburized four-point bend loaded specimens after SCC tests. In order to assess the effect of corrosion, the carburized specimen under the 0.6 mm loading level was conducted for a 24 h SCC test. The surface morphology of the specimen after SCC test is given in Fig. 7. A high amount of corrosion of the slip lines was observed. In addition, no crack on the surfaces of the specimen can be observed and no pitting occurred.

3.2.3. Cross-section investigation after SCC tests

Cross-sections parallel to the loading direction were obtained for all specimens after SCC tests and shown in Fig. 8. The cracks of the untreated four-point bend loaded specimens were mainly transgranular and branched. Furthermore, a pit was obvious on the surface of the untreated specimen under the 0.2 mm loading level and the crack initiated and propagated from the pit. However, when the untreated specimens suffered higher loading levels, the cracks were not associated with the pit. For all carburized four-point bend loaded specimens, no pits or macro-cracks were observed after SCC tests. This was in good agreement with the results of surface morphologies investigation.

3.2.4. XRD results after SCC tests

Fig. 9 gives the XRD patterns of the untreated and carburized four-point bend loaded specimens after SCC tests. The untreated specimen without external loading consisted of austenite phase before SCC tests. In addition, a weak diffraction peak of $\alpha'$-martensite was detected in the specimen, which was associated with the process of mechanical grinding [12,28]. After SCC tests, the XRD peaks of the untreated four-point bend loaded specimens were little changed.

As a result of carburization, a special phase was introduced in the carburized specimen, which is usually known as “S-phase” or expanded austenite [10]. Its peaks were broader and at lower diffraction angles than those for normal austenite in the untreated specimen. The expanded austenite was a solid solution containing a high supersaturation of carbon with a distorted fcc structure. The XRD pattern also showed some weak diffraction peaks of “$\chi$-phase” ($Fe_5C_2$) in the carburized specimen. This carbide is structurally coherent with austenite which would precipitate in highly supersaturated austenite [29]. There was no diffraction peak of $\alpha'$-martensite detected after carburization. This was because that strain-induced martensite can transform into austenite due to the dissolved carbon atoms during low-temperature surface carburization, which was demonstrated in previous work [23]. After SCC tests, almost no changes were observed for the peaks of expanded austenite under four-point bend loading was still stable for a time of 720 h in the boiling MgCl$_2$ solution at 155 ± 1 °C.

3.2.5. Stress relaxation during SCC tests

Surface stresses of the carburized four-point bend loaded specimens during SCC tests were measured to correlate the SCC behavior and carburization-induced compressive residual stresses. Fig. 10 gives the results of the carburized specimen under the 0.6 mm loading level. After 720 h SCC tests, there was still high-level compressive stress on the surfaces of the carburized specimens. Considering the measuring errors, the surface compressive stress hardly changed with the increasing time of SCC tests. This indicated that no relaxation of carburization-induced compressive residual stress occurred during SCC tests.


3.3. Improvement mechanism of low-temperature surface carburization impacts on SCC

Compared to the poor SCC resistance performance of the untreated four-point bend loaded specimens, all carburized four-point bend loaded specimens exhibited excellent resistance to crack initiation in the boiling MgCl\(_2\) solution at 155 ± 1 °C. The SCC processes of the untreated and carburized four-point bend loaded specimens are schematically illustrated in Fig. 11. The SCC behavior of each type specimen will be discussed in the terms of the experimental observation. For the untreated four-point bend loaded specimens, the top surface was in a state of tensile stress. When the tensile stress of the top surface was relatively low, the passive film rupture occurred at the defects of the surface during SCC tests, which led the formation of small pit, and the SCC initiated at the bottom of the pit where the stress concentration existed (Fig. 11(a)). However, when the tensile stress of the top surface was large enough, the SCC directly initiated at the site where the passive film breakdown occurred (Fig. 11(b)). For the carburized four-point bend loaded specimens, the top surface was still in a state of compressive stress over the whole loading range due to the presence of huge compressive residual stress which introduced by low-temperature surface carburization. As reported above, the carburized layer was highly stressed with extensive slip bands. Thus, the passive film rupture occurred at the slip bands during SCC tests (Fig. 7). However, the passive film rupture would not result in the initiation of the macro-cracks due to the presence of the surface compressive stress. In addition, the surface layer had excellent resistance of pitting corrosion due to the change of phase structure (from austenite to expanded austenite) after low-temperature surface carburization [7,8]. There were no pits on the surface after SCC tests, thereby avoiding the macro-crack initiated at the bottom of the pit. Due to low-temperature surface carburization enhanced the passive film stability [8,30], the exposed regions could be quickly passivated again. Furthermore, no relaxation of carburization-induced compressive residual stress occurred in the boil-

4. Conclusions

The effect of low-temperature surface carburization on SCC of AISI 304 ASS was investigated. Some important conclusions are:

1. Low-temperature surface carburization can significantly improve the SCC resistance of AISI 304 in the boiling MgCl\(_2\) solution at 155 ± 1 °C. During SCC tests, all untreated four-point bend loaded specimens cracked within 168 h, while the carburized four-point bend loaded specimens were tested for a total of 720 h without visual cracks.

2. The surface tensile stress of the untreated four-point bend loaded specimen and the occurrence of pits during SCC tests had detrimental effects on the SCC resistance of AISI 304.

3. The expanded austenite was stable and no relaxation of carburization-induced compressive residual stress occurred in the boiling MgCl\(_2\) solution at 155 ± 1 °C for up to 720 h.

4. The improvement of the SCC resistance of carburized AISI 304 was attributed to the compressive residual stress and the improved pitting corrosion resistance after low-temperature surface carburization. The carburization-induced compressive residual stress had the dominated beneficial effect on the SCC resistance.

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