Failure analysis of an AISI 316 steel pipe elbow exposed to the weather for three years after 16 years of operating at 515 °C

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Abstract

The failure of an AISI 316 austenitic stainless-steel pipe used in a hydrotreatment plant was investigated. Circumferential cracks starting from outside the pipe and parallel to the weld were identified in the pipe elbow. The failure occurred after three years of plant inactivity and exposure to the atmosphere. The pipe was operated regularly for 16 years at a temperature of 515 °C before failure, having undergone phase transformations that made the steel susceptible to intergranular attack, followed by stress corrosion cracking at room temperature. The preferential precipitation of chromium-rich M23C6 carbides at the grain boundaries allowed the occurrence of sensitization, which, associated with the residual tensile stresses caused by the welding process and the presence of chlorine from industrial atmosphere concentrated under insulation, were responsible for the failure by stress corrosion cracking.

Keywords: AISI 316; Pipe elbow; Stress corrosion; Failure analysis.

1 Introduction

Stress corrosion cracking (SCC) is caused by the synergistic action of sustained tensile stress (external, internal, or both) and chemical attack, causing failure in a shorter time than the individual effects would require. SCC is probably the most feared type of local corrosion because it often leads to sudden components failure without any visible changes in the metal surface. Cracks, usually initiated in some surface notches, can propagate along grain boundaries or in a transcrystalline manner in anodic (for example, in media containing halogen ions) or cathodic (such as H2S, NH3, and HCN, with the formation of hydrogen) chemical environments [1-3].

Low stacking-fault energy (SFE) face-centered cubic (FCC) metals and alloys are particularly susceptible to SCC. A low SFE obstructs the occurrence of dislocation cross-slip, decreases dislocation mobility, hinders the formation...

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of dislocation cells, leads to higher levels of internal micro-
tension, increases internal energy and Gibbs free energy, and 
leads to a greater susceptibility of the material to stress 
corrosion cracking [4,5]. Commercial austenitic stainless 
steels (ASSs) display SFEs in the range of 15–30 mJ/m², 
that is, between low and middle SFEs [6,7].

ASSs are subject to various types of corrosion 
(Table 1), such as general corrosion, pitting corrosion, 
intergranular corrosion, and stress corrosion cracking; 
however, SCC is the most frequent cause of failure in 
18Cr-8Ni austenitic stainless steels [8]. In ASSs, a strong 
correlation exists between the degree of sensitization caused 
by the precipitation of chromium-rich phases, mainly 
(Fe,Cr)₇₇₃₃₇₃, at the grain boundaries and the susceptibility 
to stress corrosion cracking [9-11].

The microstructures of ASSs are rarely fully austenitic. 
After solidification, the microstructures of the most widely 
used ASSs (AISI types 304, 304L, 316, 316L, 321, and 347) 
present delta ferrite [12], which is not entirely eliminated 
during subsequent thermomechanical processing [13]. In turn, 
the austenite phase can partially transform into two types of 
martensites (α'-bcc and ε-hcp) induced by cold deformation 
at room temperature [7,14,15].

In particular, the exposure of AISI 316 steel to 
temperatures between 500 and 900 °C can cause austenite 
to partially decompose in carbides —M₇₃C₆ and M₄C— 
and intermetallic phases —such as sigma (σ), chi (χ), and 
Laves (η)— depending on the temperature and time of the 
exposure [16-20]. These phase transformations, usually 
precipitations controlled by atomic diffusion, are often 
represented by time-temperature transformation (T4) or 
time-temperature precipitation (TTP) diagrams. For temperatures 
between 550 °C and 500 °C and exposure times longer than 
100,000 h, the TTP diagram for 316 steel predicts only the 
presence of M₇₃C₆ and possibly of Laves phase [20].

However, if 316 steel contains delta ferrite in its 
microstructure before aging, the eutectoid decomposition 
of delta ferrite stringers into sigma and austenite phases occurs 
much faster than the precipitation of the sigma phase from 
austenite because the chemical composition of ferrite is 
closer to the chemical composition of sigma phase and the 
atomic diffusion in ferrite is faster than in austenite [21,22].

Although the occurrence of SCC in ASS has been 
reported, it remains a challenge to detect and control the 
ocurrence of SCC in industrial pipes and equipment. In this 
study, we analyzed the failure of a 168.3 mm (6-inch nominal 
pipe size) AISI 316 austenitic steel pipe that operated more 
than 140,000 h (16 years) at 515 °C in a hydrotreatment 
plant before remaining for three years out of operation and 
exposed to the industrial atmosphere at room temperature.

2 Materials and methods

The chemical analysis of the materials investigated in 
this study was carried out in the laboratories of the company 
Villares Metals S. A. located in Sumaré (SP), Brazil.

The cracks in the pipe were evidenced using ASTM 
E165/E165M 2018: Standard Practice for Liquid Penetrant 
Testing for General Industry [23].

ASTM Practice A262 [24], which consists of oxalic acid 
etch test for the classification of etch structures of austenitic 
stainless steels, was used to evaluate the susceptibility to 
to intergranular attack.

Microstructural characterization was performed using 
three complementary techniques: optical microscopy (OM), 
scanning electron microscopy (SEM) combined with energy-
dispersive spectroscopy (EDS), and X-ray diffraction (XRD). 

The metallographic sample preparation consisted of 
grinding, polishing with diamond suspension of 6, 3, and 1μm 
etching. For etching a standard solution (V2A-Beize) 
was prepared by mixing 100 ml HCl, 10 ml HNO₃, and 
100 ml distilled H₂O.

X-ray diffraction analysis of the AISI 316 tube sample 
was performed using an Empyrean diffractometer (Malvern 
Panalytical) with copper tube radiation at a voltage of 45 kV, 
initial and final angles of 10° and 110°, respectively.

3 Results and discussion

Table 2 shows the chemical analysis results (weight-
percent, wt.%). of the AISI 316 austenitic steel pipe investigated.

3.1 Failure description

A 168.3 mm external diameter 7.11 mm thick 
austenitic 316 stainless steel pipe operated flawlessly for 
more than 140,000 h at 515 °C in a hydrotreatment plant.
However, high temperatures facilitated microstructural 
changes, making the material susceptible to intergranular
corrosion. Subsequently, the plant remained out of operation for three years in an industrial atmosphere, which satisfied the conditions required for crack propagation through the pipe wall.

During an inspection, through-thickness cracks initiated on the outer side (Figure 1) were detected approximately parallel to a welding bed in the pipe.

The direction of the cracks was consistent with residual stress introduced by welding and acting parallel to the weld bead.

Other locations in the pipe showed similar cracks.

Residual stresses near weld beads are frequent and can have negative or positive effects [25]. Although the pipe was exposed for a long time at 515 °C, the authors believe that the residual stresses introduced by welding were not completely eliminated by this long exposure (annealing) to high temperature. On the other hand, measurements of residual stresses were not carried out in this work. Additionally, the environment under the thermal insulation blanket (alumina-silicate ceramic fiber) can concentrate corrosive species such as Cl⁻ because of dry-water cycles originating from environmental exposure.

3.2 Cracks characterization

Figure 2 shows optical microscopy images of (a) the crack propagation along the grain boundaries and (b) the microstructure after the sensitization evaluation test using ASTM Practice A262.

Etching of the grain boundaries is accentuated as shown in Figure 2b and has been classified, according to the ASTM A262 standard: one or more grains surrounded by ditches. Semi-quantitative chemical microanalysis (EDS) inside the crack (c) shows the presence of sufficient chlorine to cause SCC in ASSs [1,2].

In our opinion, the insulation blanket was responsible for concentrating the chlorine from the industrial atmosphere on the outer surface of the pipe.

3.3 Pipe microstructure characterization

Results of pipe microstructural analysis using OM, SEM/EDS, and XRD techniques are presented below.

3.3.1 Optical microscopy analysis

Observation of the pipe by optical microscopy at low magnification (Figure 3a) reveals the microstructure of the recrystallized grains, which are apparently free of precipitates.

However, when observed at a higher magnification (1000 x), precipitation at the grain boundaries and inside the grains became evident (Figure 3b). According to the literature [16-20], the most favorable sites for the $M_n\text{C}_6$ precipitation in austenitic stainless steels are grain boundaries, followed by incoherent twin boundaries, coherent twin boundaries and finally at the dislocations within the grains.

3.3.2 Scanning electron microscopy analysis

Observation of the microstructure by SEM using backscattered electrons (Figure 4) revealed the presence of larger colonies of a second phase, or a mixture of two phases, and finer precipitates at the grain boundaries (Figures 4a and 4b), as well as the absence of precipitates on twin boundaries (Figures 4c and 4d).

3.3.3 Energy dispersive spectroscopy analysis

The EDS spectra acquired inside the colony and in the matrix are shown in Figure 5a and 5b. The higher chromium and molybdenum contents and the lower nickel content (compared to the matrix) suggest the presence of the sigma phase inside the colony. EDS was used to identify the fine precipitates at the grain boundaries (Figure 5c, d and e), as well as the absence of precipitates on twin boundaries (Figures 4c and 4d).

Table 3 summarizes the chemical compositions at the marked points (areas or spots) analyzed in Figure 5.
Figure 2. Crack propagation along grain boundaries (a) and ditch-type microstructure was performed after a test following practice ASTM A 262 (b). Analysis performed by SEM/EDS (c) showing the presence of chlorine inside the grain boundary crack (spot 1). Spot 2 showed a typical matrix chemical composition.

Figure 3. Micrographs obtained by optical microscopy after etching with V2A-Beize at (a) 200 x (b) 1000 x.

Table 3. Chemical composition (wt.%) at the points (areas/spots) analyzed in Figure 5

<table>
<thead>
<tr>
<th>Area/Spot</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.26</td>
<td>51.43</td>
<td>5.83</td>
<td>8.45</td>
<td>2.03</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>67.65</td>
<td>18.52</td>
<td>10.26</td>
<td>1.58</td>
<td>1.65</td>
<td>0.36</td>
</tr>
<tr>
<td>3</td>
<td>61.77</td>
<td>24.17</td>
<td>9.50</td>
<td>2.80</td>
<td>1.19</td>
<td>0.56</td>
</tr>
<tr>
<td>4</td>
<td>50.54</td>
<td>28.12</td>
<td>12.24</td>
<td>5.32</td>
<td>1.71</td>
<td>0.36</td>
</tr>
<tr>
<td>5</td>
<td>68.26</td>
<td>18.31</td>
<td>9.68</td>
<td>1.57</td>
<td>1.82</td>
<td>0.36</td>
</tr>
</tbody>
</table>
Figure 4. Micrographs obtained by SEM using backscattered electrons after etching with V2A-Beize. (a) General view of the microstructure; (b) Colonies containing mixed phases; (c) Grain and twin boundaries; (d) Precipitates at the grain boundaries.

Figure 5. EDS microanalysis in five positions: inside the colony – spot 1 (a); in the matrix – spots 2 and 5 (b and e), and at grain boundaries – spots 3 and 4 (c and d). See the chemical compositions in Table 3.
The analysis of the EDS spectra shown in Figure 5 and the compositions presented in Table 3, although providing relevant information about the phases present in the microstructure, did not allow for their unequivocal identification, except for the austenitic matrix.

### 3.3.4 X-ray diffraction analysis

Figure 6 shows a diffractogram of the AISI 316 tube sample. With a logarithmic intensity axis, in addition to (111) and (200) austenite peaks, low-intensity peaks in the 2θ range between 30–60° are observed. Thus, for correct identification, the range between 30–60° in the diffractogram was superimposed on the positions of the peaks of $M_23C_6$ carbide, Laves, and sigma (Figure 6b). Accordingly, Laves phase, $M_23C_6$ carbide, and sigma phase were found in the microstructure of the AISI 316 steel sample.

Deighton [29] studied the carbon solubility in AISI 316 steel between 750 and 1100 °C. According to the formula Deighton determined experimentally, carbon solubility was calculated to be approximately 40 ppm at 750 °C and practically zero at 515 °C. Therefore, all the carbon in the steel investigated in this work should precipitate during a long exposition at 515 °C to form $M_23C_6$.

Additionally, the experimental TTP diagram for exposure times longer than 100,000 h between 900 and 500 °C [20] does not support the sigma phase presence in the microstructure of AISI 316 steel at 515 °C. However, the presence of delta ferrite before exposure at 515 °C justifies the occurrence of the sigma phase for shorter exposure times [21,22].

### 4 Conclusions

During exposition at 515 °C, $M_23C_6$ ($M = \text{Cr, Fe, Ni, Mo}$) and chromium-rich intermetallic phases precipitated at the austenite grain boundaries, leading to material sensitization. Sensitization alone could not be enough to cause a tube with such robust dimensions to rupture in service. Along with this sensitization, residual welding stresses at the outer surface of the pipe contributed to developing an intergranular stress-corrosion mechanism that resulted in crack formation. Although measurements of residual stresses were not carried out in the present work, it is believed that residual stresses were not fully relieved during the long exposure at 515 °C. The propagation direction of the cracks was consistent with that of the welding residual stresses. Additionally, the environment under the thermal insulation blanket induced the concentration of corrosive agents such as $\text{Cl}^-$ ions inside the cracks. Therefore, the phase transformations at high temperatures made the steel susceptible to intergranular SCC at room temperature. However, the sigma phase detected in the microstructure is probably not related to a failure by stress-corrosion cracking.

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