Failure analysis of one peculiar ‘Yin-Yang’ corrosion morphology on heat exchanger tubes in purified terephthalic acid (PTA) dryer

Yi Gong, Zhen-Guo Yang *, Xin-Hao Meng
Department of Materials Science, Fudan University, Shanghai 200433, PR China

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A B S T R A C T

It is a common knowledge that localized corrosions occur on austenitic stainless steels such as 316L, exposed to halide ions. This paper will discuss such a localized failure that took place not long after beginning of service on the heat exchanger tubes inside a purified terephthalic acid (PTA) dryer in a petrochemical works. Particularly, one peculiar corrosion morphology termed ‘Yin-Yang’ corrosion was observed, i.e. the upside surface of the failed tubes was severely corroded while the downside was intact. Consequently, in order to ascertain the actual causes of this premature failure, samples including the failed tubes and the process media were investigated by a variety of characterization methods. Metallographic structures and chemical compositions of the tube matrix materials were inspected by optical microscope (OM) and photoelectric direct reading spectrometer; both the surfaces and the cross-sections of the corroded areas were microscopically analyzed through scanning electron microscope (SEM) and energy disperse spectroscopy (EDS); and the chemical constituents of the process media were detected via the gas chromatography–mass spectrometric (GC–MS). Finally, the localized corrosion mechanisms were discussed in detail and the pertinent countermeasures were proposed.

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1. Introduction

Purified terephthalic acid (PTA) is the raw material mainly for synthesizing the significant organic compounds as polyethylene terephthalate (PET) and poly-trimethylene terephthalate (PTT) – the matrix materials of the widely-used polyester films, fibers, bottle chips, and so on. In terms of its manufacturing process, there now exist two primary ways, the Witten and the Amoco. Comparatively, since the Amoco process consumes fewer feedstocks but yields more products, as well as facilitates higher purity of products but employs simpler manufacturing procedures, 70% PTA are produced in this way nowadays.

The Amoco process generally consists of three major steps: manufacturing CTA (crude terephthalic acid), purifying CTA to PTA, and post treatment of PTA [1]. The first step is also called the oxidation unit, and the second is the refining unit. If only focusing on the latter one, its flow chart is shown in Fig. 1. In detail, the CTA from the oxidation unit is firstly conveyed into the hydrogen atmosphere to hydrogenate the dominant impurity 4-carboxyl benzaldehyde (4-CBA) into the soluble para-toluic acid (P-TA), seen in Eq. (1). Then, in order to eliminate such P-TA, the products including both PTA and P-TA are sent into the hot water. As a result, PTA in form of the wet filter cake is obtained and transported into a dryer to evaporate the gasifiable impurities, and the dissolved P-TA is collected for recycling as well.

* Corresponding author. Tel.: +86 21 65642523; fax: +86 21 65103056.
E-mail address: zgyang@fudan.edu.cn (Z.-G. Yang).

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Apparently, the PTA dryer plays a critical role in purification of the whole manufacturing process. In our incident, such a dryer was indeed applied within a PTA plant with Amoco process in one petrochemical company in Shanghai. As for its configuration and parameters, it was a rotating cylinder (2.2 r/min) with three arrays of 3 mm-thick heat exchanger tubes inside around the circumference, and the tube diameters were 3, 4, and 5 in. respectively. From the inlet of the dryer, the high-temperature (135°C/176°C) steam vapors were conveyed in the tube side, and the wet filter cakes with PTA concentration of 38.7% were transported and heated in the shell side. From the outlet, the nitrogen gas was imported to take away the H₂O and other small molecules that were all evaporated from the wet filter cakes.

However in fact, after capacity expanding of the whole PTA plant, severe corrosion occurred on the 316L stainless steel heat exchanger tubes of the PTA dryer not long after beginning of service. Particularly, the corrosion even exhibited a peculiar morphology, i.e. the upside of the failed tubes was corroded but the downside was intact. In order to vividly depict this interesting appearance, we termed it ‘Yin-Yang’ corrosion, the well-known terminology referenced from the Chinese traditional philosophy. Correspondingly, the ‘Yin’ face was denoted as the corroded area, while the ‘Yang’ face was the intact one. Thus, for purpose of investigating the actual causes of this premature failure (designed lifetime was 8 years, failed just after 2 years), a variety of pertinent characterization measures referring to our previous experiences of failure analysis and structural integrity evaluation of heat exchanger tubes [2–9] were comprehensively employed for the samples, including matrix materials examination of the tubes, chemical constituents inspection of the process media, and macro/microscopic analysis of the defects. Results showed that the interaction between factors from the process media, the service conditions, and the operation parameters, was the main cause of this ‘Yin-Yang’ corrosion. Then, the relevant corrosion mechanisms were discussed and the countermeasures were proposed. This paper actually presents a model case of applying such comprehensive analysis methods for failure analysis in practical engineering, and its achievement will have a reference value for corrosion prevention of heat exchanger tubes operating under similar service conditions.

2. Experimental and results

2.1. Visual observation

As revealed in Fig. 2a, corrosion failure only occurred on the second array, i.e. the 4-in. tubes, of all the three arrays of heat exchanger tubes inside the PTA dryer. After sampling, Fig. 2b displayed the external appearance of the above-mentioned ‘Yin-Yang’ corrosion morphology on one failed tube, and on its surface the horizontal boundary line between the ‘Yin’ and the ‘Yang’ faces could be clearly observed. Further magnified, the corroded ‘Yin’ face was actually covered with densely distributed corrosion pits, seen in Fig. 2c, implying a localized corrosion mechanism.

2.2. Microscopic observation

For purpose of obviously comparing the two different ‘Yin’ and ‘Yang’ faces of the failed tube, Fig. 3 presented the microscopic morphologies of its cross-section. As shown in Fig. 3a, a fictitious boundary line could be drawn between the left ‘Yin’ and the right ‘Yang’ faces. Further magnified, the ‘Yin’ face was composed of corrosion concaves and pits, seen in Fig. 3b, while contrarily, the ‘Yang’ face was relatively smooth without any significant defects, seen in Fig. 3c.
2.3. Matrix materials examination

Chemical compositions of the failed tube matrix material were listed in Table 1, which met the requirements of 316L specification [10], the ultra-low carbon stainless steel with superior corrosion resistance only except to localized corrosions [11].
Fig. 4a and b displayed the metallographic structures of the ‘Yin’ and the ‘Yang’ faces respectively of the failed tube, both exhibiting typical austenitic structures with average grain size of about 6. However, it should be particularly pointed out that lots of dot-like inclusions existed within the grains, basically composed of MnS and silicon oxides, and would probably act as the initiating sites of localized corrosions when being exposed to aggressive environments [12]. Although, the material could be regarded qualified in general.

**Table 1**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Failed tube</td>
<td>0.017</td>
<td>0.398</td>
<td>0.007</td>
<td>0.030</td>
<td>1.642</td>
<td>12.158</td>
<td>16.458</td>
<td>1.997</td>
</tr>
<tr>
<td>316L</td>
<td>&lt;0.03</td>
<td>&lt;0.75</td>
<td>&lt;0.030</td>
<td>&lt;0.045</td>
<td>&lt;2.0</td>
<td>10.0–14.0</td>
<td>16.0–18.0</td>
<td>2.0–3.0</td>
</tr>
</tbody>
</table>

Fig. 4. Metallographic structures of the failed tube, 200× (a) ‘Yin’ face, (b) ‘Yang’ face.

Fig. 5. GC–MS results of the exhaust gas from CTA dryer.

Fig. 4a and b displayed the metallographic structures of the ‘Yin’ and the ‘Yang’ faces respectively of the failed tube, both exhibiting typical austenitic structures with average grain size of about 6. However, it should be particularly pointed out that lots of dot-like inclusions existed within the grains, basically composed of MnS and silicon oxides, and would probably act as the initiating sites of localized corrosions when being exposed to aggressive environments [12]. Although, the material could be regarded qualified in general.
2.4. Process media inspection

Then, in order to find out the corrosive sources of this ‘Yin-Yang’ corrosion, the process media were inspected. Since the catalysts of the hydrogenation reaction were not so aggressive (Eq. (1)), attention was only paid to the process media before the refining unit, i.e. in the oxidation unit, particularly the CTA dryer. Fig. 5 showed the GC–MS result of the exhaust gas that evaporated from the CTA filter cake in the CTA dryer. In it, the peaks at 1.34, 1.53, 2.17 and 3.46 corresponded to CH₃Br, CH₃COOCH₃, benzene (C₆H₆) and toluene (C₆H₅CH₃) respectively, while the peaks at 3.15 and 3.62 represented C₂H₂Br₂, and the peak at 6.25 was C₂HBr₃. In fact, all these substances were the by-products generated in the oxidation unit, especially because of the catalysts containing bromine element in the oxidation reaction [13]. However in terms of the refining unit, this GC–MS result positively demonstrated that most of the corrosive factors, i.e. the aggressive bromine element (ions) contained substances, had been ruled out. In other words, the ‘Yin-Yang’ corrosion inside the PTA dryer was not relevant to the process media in the service environment.

2.5. SEM & EDS

At first, surface of the failed tube with ‘Yin-Yang’ corrosion was observed under SEM. As shown in Fig. 6a, a distinct boundary line, just like that in Fig. 3a, could be easily marked between the ‘Yin’ and the ‘Yang’ faces. After magnification, lots of corrosion pits with maximum size of about 200 μm were found on the ‘Yin’ face, seen in Fig. 6b, exhibiting the familiar morphology of localized corrosions, especially pitting.

Actually, after being cut off, the cross-sections of the ‘Yin’ face further verified it was ascribed to the pitting corrosion indeed. Compared with the smooth ‘Yang’ face (Fig. 7a), the corroded ‘Yin’ face was provided with a variety of typical morphologies of pitting corrosion in theory [14], including narrow & deep (Fig. 7b), elliptical (Fig. 7c), wide & shallow (Fig. 7d), subsurface (Fig. 7e), undercutting (Fig. 7f), and horizontal (Fig. 7g). What’s more, based on the EDS results, aggressive bromide and chloride ions were detected on the corrosion products within such pits too, seen in Fig. 8 and Table 2. As mentioned above, the bromine element was the remnant from the catalyst in the oxidation reaction, nevertheless the actual source of the chlorine element still needed to be determined. Anyway, all these facts had already sufficiently demonstrated that the peculiar ‘Yin-Yang’ corrosion was led by the halide-ions-induced pitting corrosion, and its mechanisms would be discussed in detail as follows.

3. Discussion

Based on the analysis results above, it was pretty clear that localized corrosions, especially the halide-ions-induced pitting corrosion was the main cause of this peculiar ‘Yin-Yang’ corrosion on the heat exchanger tubes with qualified 316L stainless steel matrix material. Thus, it would firstly focus on the sources of the halide ions, especially the bromide and the chloride ions. As for the former one, it had been repeatedly mentioned that they were the remnant derived from the catalyst in oxidation unit. Then, how about the latter one? Since the process media in the shell side of the PTA dryer were just the filter cakes, which were theoretically free of chloride ions. So what was the source? After investigating the maintenance management, it was learnt 3% (wt%) NaOH solution was used as the alkaline wash liquor for both the CTA and the PTA dryers to eliminate the acidic scale deposits on the heat exchanger tubes’ surfaces during routine downtime, aiming to avoid crevice corrosion. However in industry, NaOH is always produced by electrolysis of saturated salt water, seen in Eq. (2), thus the chloride element will be inevitably intermingled into the NaOH products. As a result, if the 3% NaOH solution was not sufficiently purified before usage, chloride ions would be introduced, and then preferentially accumulate and attack the preexisting defects like inclusions on the tubes’ surfaces. Under this condition, localized corrosion, particularly pitting corrosion was initiated. In fact, this kind of chloride-ions-induced pitting corrosion due to inappropriate operations in maintenance management has been already discovered in our previous research on the failed CTA dryer [15].

Fig. 6. SEM micrograph of the ‘Yin-Yang’ corrosion on failed tubes. (a) Boundary line between ‘Yin’ and ‘Yang’ faces (b) corrosion pits on ‘Yin’ face.
As for the mechanism of pitting corrosion, it was so familiar and didn’t deserve repeatedly discussed in detail. Now the focus should turn to the reason why this pitting corrosion eventually brought about such a peculiar 'Yin-Yang' morphology on the failed tubes. According to the process parameters, concentration of the wet PTA filter cakes was only 38.7%, i.e. the humidity was as high as 61.3%. Meanwhile, the rotation rate of the dryer cylinder was only 2.2 r/min, a little bit lower than the designed value 2.4 r/min. Also, inside it, the motion mode of the dryer’s heat exchanger tubes was translational, rather

\[
2\text{NaCl} + 2\text{H}_2\text{O} \xrightarrow{\text{electrolysis}} 2\text{NaOH} + \text{H}_2 \uparrow + \text{Cl}_2 \uparrow
\]

Fig. 7. SEM micrograph of cross-section of the 'Yin-Yang' corrosion on failed tubes. (a) ‘Yang’ face, (b) narrow & deep, (c) elliptical, (d) wide & shallow, (e) subsurface, (f) undercutting, and (g) horizontal.
Fig. 8. EDS results of the corrosion products within pits (a) site A, (b) site B, and (c) site C.

Table 2
EDS results of the corrosion products within pits (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Mo</th>
<th>Br</th>
<th>Cl</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>2.05</td>
<td>3.19</td>
<td>1.26</td>
<td>1.55</td>
<td>1.26</td>
<td>0.81</td>
<td>17.57</td>
<td>0.93</td>
<td>61.53</td>
<td>6.66</td>
</tr>
<tr>
<td>Site B</td>
<td>2.12</td>
<td>2.76</td>
<td>1.37</td>
<td>0.90</td>
<td>1.19</td>
<td>0.50</td>
<td>15.65</td>
<td>0.92</td>
<td>67.79</td>
<td>5.36</td>
</tr>
<tr>
<td>Site C</td>
<td>1.43</td>
<td>4.69</td>
<td>2.44</td>
<td>6.70</td>
<td>0.94</td>
<td>1.91</td>
<td>44.24</td>
<td>0.60</td>
<td>30.94</td>
<td>5.59</td>
</tr>
</tbody>
</table>

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than rotational. Consequently, long-term stagnation of the pretty wet PTA filter cakes was favored on the tubes' upside surfaces due to these three factors, and then pitting corrosion was induced. With the progress of pitting corrosion, the upside surfaces were pitted and became rougher and rougher gradually, further facilitating the stagnation of the filter cakes in return. What a vicious cycle! On the contrary, it was undoubtedly that the downside was impossible to hold the wet filter cakes for a long time, so it was intact. As a result, the peculiar 'Yin-Yang' corrosion morphology was eventually formed. With respect to the reason why this corrosion only occurred on the 4-in. tubes rather than the 3- and the 5-in. ones, it may be ascribed to their different surface roughness. It could be inferred that the 4-in. tubes were not manufactured in the same batch with the other two, and coincidentally its surfaces were rougher due to unqualified treatment, then increasing the possibility of scaling for the wet PTA filter cakes.

4. Conclusions

1. Pitting corrosion occurred on the heat exchanger tubes of one PTA dryer, and even resulted in a peculiar 'Yin-Yang' corrosion morphology, i.e. the tubes' upside surfaces were severely corroded while the downside were intact.
2. Matrix materials of the heat exchanger tubes were qualified 316L stainless steels, in other words, the corrosion was not related to the incorrect selection of materials.
3. Totally six, out of all the seven typical pitting corrosion morphologies in theory were observed on the failed tubes in this incident.
4. The inappropriate operations in maintenance management, the inherent service conditions and parameters, and the unqualified surface treatment, were all the factors leading to the 'Yin-Yang' corrosion on 4-in. tubes.

5. Recommendations

1. Concentration of the chloride ions in NaOH alkaline wash liquor should be limited under 30 ppm to avoid pitting.
2. Amount of the catalysts that contain bromine element in the oxidation unit should be strictly controlled.
3. Surface conditions of the 4-in. tubes must be inspected, and adequate treatment should be carried out if necessary.

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References