Study of Reasons for Pitting Corrosion Occurred on Flange Made of 1Cr18Ni9Ti Stainless Steel

Gang Sun¹, Xiaolin Li¹, Jun Du², Jia Luo¹ and Tairan Wang¹
¹Beijing Institute of Structure and Environment Engineering, Beijing, China.
² Beijing Institute of Electronics System Engineering, Beijing, China.
Email:181709810@qq.com

Abstract. When pickling the stainless steel flange made of 1Cr18Ni9Ti after welding process, rough pits were observed on the surface of the part. An investigation of occurrence mechanism and chemical composition of these pits has been carried out, which involved scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS). It was found that the flange suffering local corrosion called pitting corrosion during the pickling process, for the reason of that cavities occurred between the outer sleeve nut and the weld joint area blocked the movement of cations, mostly Fe³⁺ and Cr³⁺. These cations hydrolyzed to H⁺ absorbing Cl⁻ outside the cavity in the pickling acid causing corrosion on the part surface. Adjusting purity of pickling acid and shafting the part during pickling process can obviously reduce the potential of occurrence of pitting corrosion.

1. Introduction
Among various types of stainless steel, austenitic stainless steel with chromium and nickel as main alloying elements is the best corrosion resistance and comprehensive performance, and it is also the most important stainless acid-resistant steel [1]. The representative steel of 18-8 steel type is 1Cr18Ni9Ti steel which commonly used in industry. The main danger of austenitic stainless steel in use is local corrosion especially pitting corrosion [2, 3]. This corrosion usually occurs in the cavity formed between surfaces of metal and metal or metal and nonmetal which immersing in electrolyte. like connecting area between flange and flange, gasket and bolt, twisted area between metals. This corrosion can lead to cracks or even penetrations occurring on the surface of the part [4]. This phenomenon result in deducing strength of part or deteriorating the fitting tolerance of the parts, sometimes even causing damage accident [5].

1Cr18Ni9Ti stainless steel has good performance in welding process, but of which products made are susceptible to grain corrosion in acid environment. For some product with abnormal geometry in case of welding process involved, we have to use this material to take advantage of good welding performance, at the same time we must pay attention on corrosion issues especially.

The flange butt welded pipe shaft made of 1Cr18Ni9Ti stainless steel compose the product called spherical joint which, matching with outer sleeve nut, can connect two different diameter size pipe. after the welding process, the product will be pickled to remove the welding oxide layer on the surface of the welded area. After pickling, the flange is found that near the end of the weld, the surface matching the outer sleeve nut is rough and pitted. This paper analyzes the rough surface by using metallographic microscope, scanning electron microscope (SEM) and energy spectrum analyzer (EDS). Finally, the reason for the rough and pitted surface of the spherical joint is determined, and the cause of failure is discussed, which can provide an important reference for preventing pitting corrosion of similar materials.
2. Materials and Methods

2.1. Visual Observation

Visual observing the pit on the flange, we found that corrosion occurs at the point where the flange contacts the outer sleeve nut. The center of the corrosion is about 10mm from the center of the weld (shown in figure 1). The corrosion is about 7mm wide and 26mm in length. The perimeter is about 2/5. Observed under a stereo microscope, the corrosion has two morphological features. One is the appearance of corrosion pits of different sizes with a deeper depth. The other is the larger area of the corrosion area but with a shallower depth (shown in figure 2). No corroded morphology was seen on the weld and the pipe butt jointed with the flange. The inner surface of the matching nut is smooth and no corroded morphology was found.

![Figure 1. The position of corrosion.](image1)

![Figure 2. Magnify macrograph of corrosion.](image2)

2.2. Analysis by SEM and EDS

Observed the surface of the part under the scanning electron microscope (SEM), the surface of the corrosion area is relatively clean (shown in figure 3) compared to the pit in the corrosion area (shown in figure 4), and no morphology of the corrosion product have been seen. analyzing chemical composition by Energy Dispersive Spectroscopy (EDS) in the pit in the corrosion area, shallow corrosion area and the healthy area with no corrosion, we found that Fe, Cr, Ni elements are most been found in these three areas, and shared almost same portion in total of the weight(shown in table 1). EDS showed that no metallurgical defects such as inclusions and segregation were found in the corroded area of the flange.

![Figure 3. Pattern of surface on corrosion in SEM.](image3)

![Figure 4. Pattern of pit in corrosion in SEM.](image4)
Table 1. Chemical composition of pit by EDS (wt.%).

| Position                        | Si  | Ti  | Cr  | Mn  | Fe  | Ni  |
|---------------------------------|-----|-----|-----|-----|-----|-----|
| pit in the corrosion area       | 0.79| 0.47| 19.83| 1.33| 67.76| 9.82|
| shallow corrosion area          | 0.69| 0.48| 19.66| 1.96| 67.52| 9.69|
| healthy area with no corrosion  | 0.72| 0.68| 18.89| 1.68| 68.47| 9.57|

The chemical composition analysis by EDS was also performed on the flange and the matching outer sleeve nut. The chemical composition comparison between flange, the matching outer sleeve nut and criterion of GB/T1220-2007 is shown in Table 2. It is turn out that this material is 1Cr18Ni9Ti, and the chemical composition meets the requirements of GB / T1220-2007.

Table 2. Chemical compositions comparison (wt.%).

| Position                | C     | S     | P     | Cr    | Ni    | Ti     | Mn     | Si     |
|------------------------|-------|-------|-------|-------|-------|--------|--------|--------|
| flange                 | 0.048 | 0.001 | 0.012 | 18.11 | 9.878 | 0.326  | 1.55   | 0.972  |
| outer sleeve nut       | 0.051 | 0.001 | 0.012 | 17.95 | 9.93  | 0.282  | 1.513  | 0.588  |
| GB/T1220-2007          | ≤0.12 | ≤0.030| ≤0.035| 17.00-19.00| 8.00-11.00| 5(C%-0.02)-0.80| ≤2.00 | ≤1.00 |

2.3. Metallographic Analysis

Metallographic specimens cut from the flange and the matching outer sleeve nut in the axial direction were examined using an metallographic microscope. It is showed that the structure in the corrosion site is a pure austenite structure with a grain size of 8 (shown in figure 5), the maximum depth of this structure is about 160 μm, and no inclusions have been seen in the pit area. While the matching nut also has a pure austenite structure with the grain size of grade 6 (shown in figure 6).

![Figure 5. Microstructure of the corrosion.](image)

![Figure 6. Microstructure of outer sleeve nut.](image)

3. Discussion

In summary, the surface of the flange has obvious characteristics of pitting corrosion of the stainless steel. Pitting usually occurs in specific corrosive solution containing halogen anions of which chloride and bromide harmful most. It is usual in localized corrosion of stainless steel [6].

In austenitic stainless steel, smaller grains with more grain boundaries cause structure inherit a worse corrosion resistance [7], when austenitic stainless steel be heated to 400 ~ 800 °C after a solid solution treatment, the chromium carbides in the steel precipitated more intensely, making the steel more sensitive to corrosion. This temperature is called the sensitization temperature [8]. The austenite grains be heated to a degree higher than sensitization temperature inherits a worse corrosion resistance than that of the austenitic grains only treated by means of solid solution.

In this structure, the flange is connected to the pipe by means of welding. During welding possess, temperature of welding range from 600° C to 1000° C is higher than sensitization temperature, causing the welding heat affected area inherits more sensitive to corrosion than that in other area. In addition, because of the grain size of the flange is grade 8 and the outer sleeve nut is 6 grades, the flange is weaker in corrosion resistance than the outer sleeve nut.
In the electrolyte, the movement of related substances in a narrow cavity formed between metal and metal or metal and non-metallic surfaces is blocked, produce a concentration cell phenomenon, resulting local corrosion. This corrosion is called pitting corrosion.

The purpose of pickling this part is to remove the oxide scale layer around the weld metal after welding process. In the process of pickling, the parts are directly immersing into the pickling solution keeping a static position, and the outer sleeve nut of the parts directly contacts the welding area of the flange and nozzle. During the pickling process, a cavity formed between the outer sleeve nut and the weld joint area of the flange and the nozzle. Because the part remains unmoved in this process, cations, mostly \( \text{Fe}^{3+} \) and \( \text{Cr}^{3+} \), occurred in this process hardly diffuse out of the cavity, as shown in figure 7.

![Figure 7. The sketch map in the pickling acid.](image)

As a result these cations undergoing the following hydrolysis in the cavity [9]:

\[
\begin{align*}
\text{Cr}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Cr(OH)}_3 + 3\text{H}^+ \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+
\end{align*}
\]

Cations hydrolysis will eventually lead to a sharp increase in the acidity (H⁺) inside the cavity, resulting a large number of anions (such as Cl⁻) will be adsorbed from the outside of the cavity. However, the corrosion resistance of the heat affected zone of the flange is relatively weak, so the occurrence of high concentrations of H⁺ and Cl⁻ in the cavity causes severe corrosion in the cavity, which eventually appears as pitting corrosion morphology on the flange.

Pitting corrosion in cavity is a complicated process, and its formation and production are affected by many factors such as geometry and environments. Usually part geometry cannot be changed to improve corrosion situation, but we can focus on changing environmental aspects to achieve this purpose.

As we analysis the pickling process of this part, we learned:

1. During the pickling process, reused acid is continuously returned to the pickling bath with next new part undergoing this pickling process resulting amount of waste is dramatically produced.

2. During the pickling process, the part maintains a static position resulting a cavity formed between outer nut and weld zone of flange and nozzle. which blocked the movement of anions and cations, leading to corrosion occurs in this cavity.

In order to reduce the potential of pitting corrosion of this part during the pickling process, we suggest:

1. Strictly monitoring the content of the pickling acid solution make sure that the harmful impurities generated in the solution are promptly cleaned up or replacing them regularly.

2. Part should be turned during pickling process. preventing the cations in cavity accumulated which can obviously reduce the potential of pitting corrosion occurs.

4. Conclusions

The analysis by EDS showed that the material composition meets the requirements of the 1Cr18Ni9Ti composition in GB / T 1220-2007. The metallographic analysis showed that the structure of the material is pure austenite structure, which meets the metallographic structure characteristics of 18-8 stainless steel.
The corrosion properties on the flange surface are pitting corrosion morphology caused by corrosion in the cavity formed in the part. During the pickling process, the part maintains a static position resulting in a cavity formed between outer nut and weld zone of ball joint and nozzle which blocks the movement of anions and cations, leading corrosion occurs in this cavity. In order to reduce the potential of pitting corrosion of this part during the pickling process, we can:

1. Strictly monitoring the content of the pickling acid make sure that the harmful impurities generated in the solution are promptly cleaned up or replace them regularly.
2. The part should be turned during pickling process, preventing the cations in cavity accumulated which can reduce the potential of pitting corrosion.

5. References

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