Cause Analysis of Flat Concave Defects on the Inner Surface at the end of T91 Alloy-Steel Tubes

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Abstract. The concave defects on the inner surface at the end of T91 alloy-steel tubes were analysed by macroscopic morphology analysis, electron microscope scanning and energy spectrum analysis, metallographic analysis and anion analysis of corrosion products. The composition of water sample and oil sample of finned winding and oil immersion treatment was also analysed. It was found that this kind of defect was not caused by the preservation environment of steel tube, the treatment of finned winding and oil immersion. The defect should be related to the quality of steel tube blank or the processing technology of steel tube.

1. Introduction
A batch of T91 seamless tubes were stored for more than half a year, after finned winding, it is found that there are flat concave defects on the inner surface at some steel tube ends. The manufacturing standard of this batch of tubes is ASME SA-213M 2015\(^{[1]}\). During the whole cycle of the formation and existence of this flat concave defects on the inner surface, the steel tubes have gone through the processes of billet smelting, cold drawing processing, storage and preservation, finned winding and oil immersion rust prevention, etc\(^{[2]}\). The formation of the flat concave defects in steel tubes must be directly related to one or more of the above processes. In this paper, the effects of steel tube preservation environment, finned winding and oil immersion treatment on the formation of defects are analysed.

2. Macro Morphology Analysis of Internal Surface of Steel Tube
There is obvious corrosion phenomenon on the inner surface of the tube end, and there are a large number of flat concave defects in the uniform distribution as shown in figure 1.
The corrosion products on the inner surface of the steel tube are reddish-brown, and no other forms of corrosion products are filled in the concave, and after local grinding on the inner surface, concave defects are still visible. The total length of the steel tube is 22 meters. The corrosion of the inner surface of the steel tube is slight at its 1/3 and 1/2 locations. After local grinding, the inner surface is smooth, and no concave-like defects are found.

3. Metallographic Analysis
The corrosion products on the surface of the sample were removed by pickling, and the macroscopic morphology and metallographic structure were analysed. The results show that the bottom and edge of the concave section transition smoothly, and there is no uniform expansion of the defect to the wall thickness. The microstructure is normal tempered martensite, no non-metallic inclusions are found, and the grain size is 10, as shown in figure 2 and figure 3.

4. Electron Microscopic Scanning and Energy Spectrum Detection and Analysis of Defect Sites
The defect site of the sample was detected and analysed by electron microscope scanning and energy spectrum as shown in figure 4 and figure 5. It can be seen that the defect of the concave is approximately circular, the bottom of the concave is relatively flat, and the edge of the concave is irregular crack morphology. Under the electron microscope, Areas 4 and 5 are in the concave, areas 1, 2 and 3 are at the boundary of the concave, and area 6 is outside the concave. The results of the energy spectrum detection are similar. The black areas are mainly metal matrix and its oxides, which contains a small amount of Cl⁻ or does not contain Cl⁻. The white area showed crystal structure under electron microscope, compared with the black area, the local concentration of Cl⁻ was found in the white area, but no enrichment of Cl⁻ was found inside and outside the concave.
5. Analysis of Water Sample and Oil Sample of Fin Winding and Antirust Treatment by Soaking Oil

In the process of finned winding and oil immersion antirust treatment, the outer surface of the steel tube is directly in contact with cooling water and antirust oil, and the inner surface of the steel tube is likely to be in small contact with cooling water and antirust oil. The cooling water is used for recycling. The cooling water is sampled and analyzed in three periods of the day. At the same time, two parts of antirust oil are selected for composition analysis. It is found that both water and oil samples are weakly alkaline, and the composition is not obvious abnormal as shown in table 1.

![Energy spectrum detection and analysis of defect sites](image)

**Figure 5.** Energy spectrum detection and analysis of defect sites
Table 1. Analysis of water sample and oil sample

|                | Cl⁻ (mg/l) | SO₄²⁻ (mg/l) | NO₃⁻ (mg/l) | pH | Na (mg/l) | Al (µg/l) | Fe (mg/l) | Hardness of water (mg/l) |
|----------------|------------|--------------|-------------|----|-----------|-----------|-----------|-------------------------|
| Water sample 1 | 41.2       | 58.2         | /           | 7.2| 54.0      | 2.92      | 0.23      | 159                    |
| Water sample 2 | 61.4       | 87.8         | /           | 7.8| 48.0      | 4.37      | 0.21      | 155                    |
| Water sample 3 | 61.8       | 88.0         | /           | 7.5| 50.4      | 1.57      | 0.22      | 165                    |
| Oil sample 1   | 28         | /            | /           | 7.5| 87.0      | /         | 7.0       | 220                    |
| Oil sample 2   | 18         | /            | /           | 7.2| 83.0      | /         | 9.0       | 235                    |

6. Anion Analysis of Corrosion Products

The anions of corrosion products were analysed by ion chromatography as shown in table 2. The results showed that the specific gravity of anions in corrosion products was very small and the samples were not exposed to corrosive acidic substances for a long time.

Table 2. Anion analysis of corrosion products

| Wight of sample (g) | F⁻ (%)   | Cl⁻ (%)   | NO₃⁻ (%)  | SO₄²⁻ (%) | Br⁻ (%) |
|---------------------|----------|-----------|-----------|-----------|---------|
| 0.044               | 0.017273 | 0.096477  | 0.022727  | 0.045     | 0       |

7. General Analysis

It has been confirmed that the steel tubes are superimposed and stored in the indoor standard warehouse with roof and indoor air circulation. There is no corrosive atmospheric atmosphere such as acidity in the environment of the area, and the sampling tubes are located in the middle and upper parts of the superimposed steel tubes. In the normal preservation process, the possibility of direct contact between the sample tube and the corrosive medium is relatively small. The flat circular concave defects are evenly arranged on the whole inner surface of the tube end, and there is no corrosive waterline on the inner surface, if the concave is caused by environmental oxidation corrosion. There should be multiple volume expansion corrosion products on the concave, but the results of macroscopic morphology examination of the inner surface show that there is no corrosion product filling on the concave, which does not belong to the typical environmental oxidation corrosion morphology. Therefore, the concave should not be directly caused by environmental oxidation corrosion, and the preservation environment will not directly lead to the emergence of concave defects on the inner surface of the end of the steel tube.

The concave defects on the inner surface of the steel tube only appear at the end of the steel tube, and there are no such defects on the inner surface of the other finned wound parts, such as the inner surface of the steel tube 1/3 and 1/2 locations, which indicates that the finned winding process does not directly lead to the concave defects on the inner surface.

Through metallographic analysis, it can be seen that the metallographic structure of the steel tube in the finned part is normal, which indicates that the finned processing technology has no adverse effect on the metallographic structure of the steel tube.

Through energy spectrum detection and anion analysis, it is found that the main anions in the corrosion products are Cl⁻ and SO₄²⁻. Through the analysis, it can be seen that:

- The concave defects at the end of the steel tube are approximately circular, the bottom of the concave is relatively flat, and there is no enrichment of Cl⁻ in the inner and outer regions of the concave. At the same time, from the metallographic morphology of the concave section, it can be seen that the bottom and edge of the concave transition smoothly, there is no cracking. It was also not observed that the corrosion persistence caused by the enrichment of Cl⁻ was unitarily extended to the metal wall thickness.
- Both water and oil samples were weakly alkaline, and a small amount of SO₄²⁻ would only adhere to the metal surface. It does not directly lead to corrosion of metal matrix.
• The anion analysis results of corrosion products show that the specific gravity of anions in corrosion products is very small, so the samples are not exposed to corrosive acid substances for a long time. The corrosion products are mainly iron oxides. Therefore, the existence of a small amount of \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) is not the main factor leading to corrosion.

8. Conclusion
Through the above comprehensive analysis, it can be seen that the preservation environment of the steel tube, the processing technology of the fin winding, and the contact process between the cooling water and the antirust oil will not lead to the concave defects on the inner surface of the end of the steel tube. The occurrence of this defect should be related to the quality of steel tube blank or other links or factors such as steel tube processing technology.

References
[1] ASME SA-213M 2015 *Standard Specification for Seamless Ferritic and Austenitic Alloy-Steel Boiler, Superheater and Heat-Exchanger Tubes* (New York: The American Society of Mechanical Engineers)
[2] Caifu Wang 2014 *Research on the Corrosion Behavior and Surface Modification of T91/T92 steel* (Nan Chang: Nanchang Hangkong University)