Analysis and Life Evaluation of CS₂ Reaction Tube

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Abstract: The chemical composition analysis, macro and microstructure analysis, mechanical properties and other methods were used to analyze the state and life of CS₂ reaction tube for a period of time. The results showed that there is no sulfur corrosion ditch in the furnace tube, and the other one has a uniform corrosion state except for the severe local corrosion. The mechanical properties are good at room temperature. The number and appearance of σ phase are the main reason for making material brittle, welding property degradation and causing crack. The approximate residual life of the furnace tube is also evaluated by various means analysis and life calculation. It is recommended that the tube be replaced with a higher grade nickel-chromium alloy instead of HK40.

1. Introduction

The main components of the reactor tube material is the nickel-chromium, the mass fraction of 20% and 25% of nickel-chromium alloy steel has been used for CS₂ reaction tube materials which can withstand high temperature of 1050°C. With the updating and optimization of petrochemical processing technology, the alloys and can withstand high temperature 1100°C [1]. The reaction tube is made by centrifugal casting method and smooth inner surface machining process is to reduce the reaction of coke [2]. The CS₂ reaction radiant tubes were used for 18 months in which the three of them were severe failure. The three tubes were analyzed respectively, the one is under the eastern side of the 8th layers of a furnace (also called tube 1), another one is in 2th layer of bottom of the west side (called tube2) and the 15th layer one (called tube3).

2. Test Results and Discussion

The spectral analyzers, metallographic microscope and other equipment are used to research the cracked tube section. The comprehensive analysis will be done to find out the failure reasons.

2.1. Chemical Composition

The chemical composition analysis in Table 1 shows that the carbon mass fraction and common elements Si, Mn, P and S satisfy standard requirements [3].

| Sample | C  | Si  | Mn  | S   | p  | Cr  | Ni  | Mo  | Fe  |
|--------|----|-----|-----|-----|----|-----|-----|-----|-----|
| Tube 1 | 0.45 | 1.02 | 1.11 | 0.0264 | 0.00677 | 26.32 | 33.93 | 0.0506 | other |
| Tube 2 | 0.438 | 0.941 | 0.892 | 0.0213 | 0.0113 | 25.70 | 20.93 | 0.0468 | other |
| Tube 3 | 0.413 | 0.976 | 0.987 | 0.0171 | 0.016 | 24.53 | 20.53 | 0.0381 | other |
| Standard | 0.35-0.45 | ≤1.5 | ≤1.5 | ≤0.03 | ≤0.03 | 24/28 | 34/37 | ≤0.5 | other |
2.2. Macrostructure Inspection
The result of Penetrant inspection is shown in Figure 1 a, b, c respectively. Figure (a) is the inner surface of the tube No. 1 for selective corrosion and appears pit. The inner surface of pipe 2 is basically uniform corrosion in Figure (b). Figure (c) is the No. 3 crack pipe ring.

The past many cases show that a more serious sulfur corrosion groove was found in the inspection and assessment process for CS$_2$ reaction furnace tube serviced for many years. But the analyzed furnace pipes were not found to have sulfur corrosion groove.

![Figure 1. The penetration inspection results of three tube](image1)

The diameter and wall thickness of furnace tube are measured. The standard size of the furnace tube is $\Phi$168×14. Measurement results showed that the outer diameter size within the manufacturing error range. The diameter size of three furnace tubes is slightly larger than the standard size. The varying degrees of corrosion results in uneven wall thickness.

2.3. Microstructure
The microstructure the matrix of the three furnace tube shows in Figure 2a, b, c, respectively, a eutectic carbides state remains intact in the microstructure, the secondary carbides is small and diffused, and there is a small amount of acicular $\sigma$ phase. The state of carbides in tube 1 and tube 3 is basically the same, the number of needle-like $\sigma$ phases to tube 3 is relatively small. Microstructure analysis for three tube used for a period of time shows that the eutectic carbides change little, which still maintain a better state and the secondary carbides are fine and dispersed which are in good condition. Precipitation of a large number of needles $\sigma$ phase which is a hard and brittle leads to lower plasticity. This is the root cause of reduced weldabilit.

![Figure 2. Microstructure of the matrix of three tube](image2)  oxalic acid electrochemical corrosion

2.4. Damage of Internal and External Surface of Furnace Tube
The external surface corrosion is slight by detection for the three tube ring. The damaged layer within 0.5mm, including the transition layer. In Figure 3, a, b and c are the outer surface microstructure of the tubes 1, 2 and 3, respectively.
Figure 3. The microstructure of the outer surface of the three furnace tubes Oxalic acid electrolytic corrosion

Figure 4. The microstructure of the inner surface of the furnace tube Oxalic acid electrolytic corrosion

The local severely corroded part of tube1 is in Figure 4 (a), the more uniform corrosion sites in tube1 was shown in Figure 4 (b). The corrosion of the inner surface of tube 2 and tube 3 are shown in Figure 3c and Figure 4d respectively. The corrosion of inner surface of tube2 and tube3 is uniform.

2.5. Mechanical Property Analysis and Life Assessment

The mechanical properties of three kinds of furnace tubes at room temperature and high temperature were tested. The results show that the strength of the material is very good, Plasticity decreased. The results meet technical contact requirement.

In this detection, the corrosion of the furnace tube1 is the most serious, so the furnace tube will be used to evaluate the remaining life. With the more serious corrosion, its effective wall thickness will be reduced, which will cause the furnace to bear the stress increased, the corresponding P value decreases, the residual life of the tube will also be reduced, In this paper, the medium diameter formula and L-M curve are used to evaluate the life [4].

The design of the furnace tube diameter 168mm, Wall thickness 14mm, The design pressure is 0.9MPa and the applicable temperature is 820 ~ 860°C. Furnace tube measured temperature between 706 ~ 841 ºC. For safety, the temperature used for life prediction is 860°C. Measured maximum corrosion layer thickness of 6.4mm, used time is the 15 month (40,000hrs), the corrosion rate calculated by uniform corrosion is 0.356mm per hour. According to HK40 alloy L-M curve of $P = T \times (15 + \log tr) \times 10^{-3}$ formula, P value for 40,000 hours is 22.21, L-M curve corresponding to its lower limit stress is 18.7MPa [5], the 80% of the stress is 15.0MPa as shown in Figure 5. According to the relevant provisions of GB150-2011 and JB4732-1995, the furnace tube in this paper belongs to the internal pressure cylinder equipment, the main stress can be obtained by the following formula

$$\sigma = \frac{P_0 - \phi_m}{2\Phi_M} (1-1).$$

$P_0$: tube design pressure, MPa;
$\Phi_M$: the value of the tube diameter minus the effective wall thickness, mm
W: Effective wall thickness mm
The measured minimum wall thickness is 14-6.4=7.6mm. The outer surface corrosion layer is 0.5mm and that of the inner surface is 1mm. The minimum effective wall thickness for calculation is 6.1mm. The safest minimum wall thickness for 40,000 hours can be calculated by the formula (1-1) is 3.88mm. Safe and effective wall thickness of only 6.1-3.88 = 2.22mm, according to the corrosion rate of 0.356mm / month, the tube safe use of time only 6 months.

3. Conclusion
None of the three tubes was found to have sulfur corrosion ditches. Good mechanical properties, the strength index is good and is higher than the standard, the plastic properties of materials decreased. The eutectic carbides remained in a good condition by microstructure analysis. The secondary carbides are small and divergent and have a large amount of needle-like σ phases precipitated. Needle-like σ-phase precipitation leads to the material brittle and cracks and welding property decreased. The inside of the furnace tube contacts the reaction gas and the outside contacts the combustion air. Usually furnace tube are bear high temperature, internal pressure, weight, other stress, as well as repeated low-cycle fatigue caused by the parking[6]. In order to improve its high temperature corrosion resistance and high temperature strength should be replaced with a higher level of nickel-chromium alloy.

![Figure 5. The L-M curve of HK40 alloy and evaluated point of remaining life](image)

4. References
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