

Discussion on Repair Technology of Zinc Oxide Desulfurization Reactor

Bo Yang*

Shanghai Institute of Special Equipment Inspection and Technical Research, Shanghai, 200062, China

**Corresponding author: yangbo@ssei.cn*

Keywords: Desulfurization reactor; Crack repair; Heat treatment; Nondestructive testing

Abstract: During the inspection of zinc oxide desulfurization reactor in an oil refining reconstruction project, it was found that there was a suspected crack in the weld of the reactor body. Because the main material of the equipment is 15CrMoR, hardened microstructure is easy to be produced during welding, and hydrogen-induced delayed cracks are easy to occur in welded joints due to the combined action of sufficiently high diffusion hydrogen concentration in the weld zone and certain welding residual stress. The user and the original manufacturer made a repair plan, scientifically and reasonably repaired the cracks, and used them after being confirmed to be qualified by nondestructive testing.

1. Introduction

The zinc oxide desulfurization reactor of a company's 55,000-ton/a hydrogen production plant is made of 15CrMoR(H), with a specification of $\phi 2200 \times 52 \times 17820$, a design pressure of 4.5 MPa, a design temperature of 420°C and a working medium of feed gas. This equipment belongs to Class III pressure vessel. It was manufactured in March 2020 and officially put into use in December 2020.

2. Defects Found by Inspection

According to TSG 21-2016 Safety Technical Supervision Regulations for Fixed Pressure Vessels in 8.1.6.1, pressure vessels are generally inspected regularly for the first time within 3 years after being put into use. ^[1]In November, 2023, during the first comprehensive inspection of the equipment, a zone III reflection was detected by ultrasound at the weld B2 of the body, which was located on B2, 1370mm away from the A2 T-joint, as shown in Figure 1. According to the original manufacturing data and the appearance of weld on site, it is determined that this place has been repaired twice during manufacturing. The reflection at this place was rechecked by TOFD and phased array, and the X-ray film at the time of manufacture was reviewed, and it was determined that the defect was a suspected crack. The defect length is 15mm, its height is 12mm, and the display depth is 39mm.

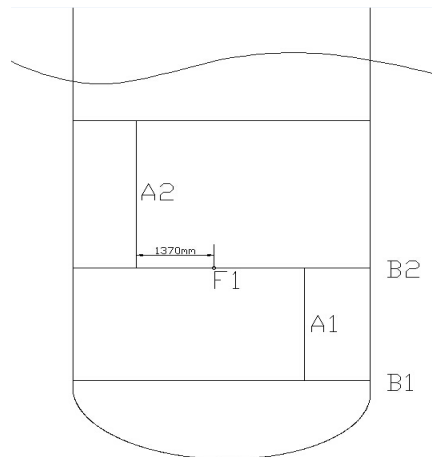


Figure1: Schematic diagram of defect location

3. Defect Cause Analysis

3.1. Weldability Analysis of 15CrMo Steel

The main material of the equipment, 15CrMoR(H), belongs to low-alloy heat-resistant steel with the mass fraction of alloying elements ranging from 1.33% to 3.13%. The main alloying elements Cr and Mo can significantly improve the hardening capacity of the steel. These alloying elements delay the transformation of the steel in the cooling process, improve the stability of undercooled austenite, and are not easy to decompose, but martensite transformation occurs at lower temperature.

When materials are welded, hardened microstructures are easily formed at a high cooling rate, and hydrogen-induced delayed cracks are easy to occur in the welded joint due to the high enough diffusion hydrogen concentration in the weld zone and certain welding residual stress ^[2-3], which are more likely to occur in the heat affected zone and weld metal. This kind of cold crack is the main danger in welding Cr-Mo steel. The production practice and theoretical research show that ^[4-5]: the hardening tendency of steel, hydrogen content and its distribution, and the state of constraint stress are the three main factors that cause cold cracks in high-strength steel.

In addition, the weld tends to form hot cracks because of the narrow and deep pear-shaped weld bead, and the low melting point eutectic is concentrated in the center of the weld bead, which leads to hot cracks in the center of the weld bead under the action of welding stress. Therefore, it is necessary to take appropriate technological measures and choose appropriate welding materials during welding to avoid such cracks. ^[6-7]

3.2. Manufacturing Legacy Issues

According to the original data, cracks were detected in the parts where cracks were found during factory manufacturing, and the reason was that the heat treatment procedures were not implemented according to the plan. After the second repair, RT, UT, MT and other nondestructive tests were carried out after the repair, heat treatment and water pressure. No defects were found at that time, and they passed the inspection and left the factory.

3.3. Causes of Defects

Through the analysis of the welding performance and original manufacturing data of the

materials, it is concluded that the performance of the materials themselves and the "hidden dangers" left over in the manufacturing process have caused the reactor to crack again in the same part after three years of use.

4. Repair Plan and Treatment

4.1. Compilation Basis

According to TSG 21-2016 Safety Technical Supervision Regulations for Fixed Pressure Vessels, GB150-2011 Steel Pressure Vessels, NB/T47014-2011 Welding Procedure Qualification for Pressure Equipment, NB/T47015-2011 Welding Regulations for Pressure Vessels and NB/T47013-2015. According to the relevant provisions of Technical Requirements for Manufacturing Steel Chemical Containers (HG20584-2011) and Post-weld Heat Treatment Regulations for Pressure Equipment (GB/T30583-2014), the user and the original manufacturer have formulated a repair plan.

4.2. Dehydrogenation Treatment Before Welding

In order to ensure the effect of hydrogen elimination treatment, the whole circle of B2 weld is heated. The outer side is paved with an electric heating sheet with a width of 300mm. Electric heating plates shall be laid at the defective parts of the inner ring, and the length and width of the electric heating plates shall not be less than 300mm. The whole circle outside and the covered parts of the inner electric heating sheet are covered with thermal insulation cotton, the width of which is 600mm and the thickness of which is 100 mm.. Dehydrogenation temperature is 350-400°C and heat preservation time is 4 hours. After dehydrogenating treatment, the whole weld is insulated after the temperature is reduced to 180-200°C. Ensure that the preheating temperature of the defect part is 180-200°C when the defect is eliminated.

4.3. Eliminate Defects

The defects are removed by grinding from the inner surface with the grinding depth of 15mm-20mm, until the defect parts and their surrounding areas show metallic luster, and then carry out visual inspection. After the defects are confirmed clearly, MT inspection is carried out. The inspection standard is NB/T47013.4-2015, which is Grade I qualified. The whole process of grinding requires that the preheating temperature be controlled at 180-200°C.

4.4. Repair Welding

The repair welding adopts covered electrode arc welding, and the welding material is covered electrode R307C specially used for 15CrMoR(H) steel of Will Company. The welding material specification is ϕ 3.2 and ϕ 4.0 covered electrode. See Table 1 for the welding specifications.

Table 1: Welding process

	Electriccurrent	Voltage	Welding speed
Φ 3.2	90-120A	20-24V	100-200mm/min
Φ 4.0	140-170A	22-26V	120-200 mm/min

The preheating temperature of welding is 180-200°C, and the temperature between tracks is 180-250°C. In order to ensure the welding quality, skilled welders with rich experience are selected for repair. Welders have relevant qualifications, and the welder's post project is

SMAW-FeII-2G(K)-12-Fef3J.

In the process of repair welding, the welder measures the inter-pass temperature of each weld to ensure that it meets the process requirements.

After welding, after visual inspection is qualified, MT inspection shall be conducted immediately, and the inspection standard is NB/T47013.4-2015, with Grade I qualification.

4.5. Dehydrogenation After Welding

After passing the post-welding inspection, the hydrogen shall be removed immediately. Dehydrogenation temperature is 350-400°C and heat preservation time is 2 hours. The arrangement and covering requirements of heating sheet and thermal insulation cotton for post-welding hydrogen elimination treatment are the same as those for pre-welding hydrogen elimination treatment.

4.6. Flaw Detection

The flaw detection shall be carried out 24 hours after hydrogen elimination, and the repaired parts shall be subjected to nondestructive testing. RT is required to be 100% Grade II qualified and MT is required to be 100% Grade I qualified.

4.7. Heat Treatment

After the NDT is qualified, the B2 weld is subjected to full circle local heat treatment. Two thermocouples are evenly distributed at the repair site and the opposite weld, and heat treatment is carried out according to the following heat treatment curve. The arrangement and covering requirements of heating sheet and thermal insulation cotton during heat treatment are the same as those of hydrogen elimination treatment before welding, and the heat treatment process is shown in Figure 2.

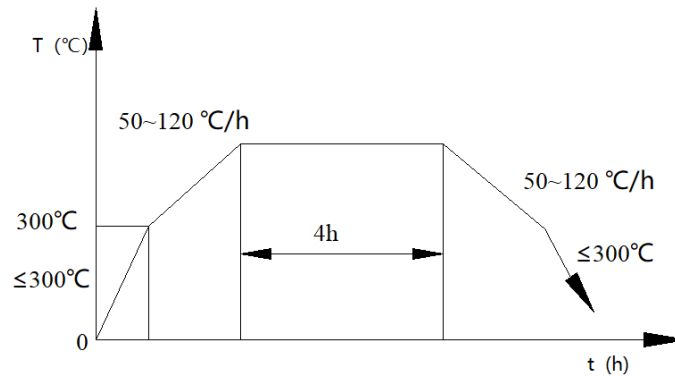


Figure 2: Heat treatment process

Finally, nondestructive testing was carried out on the repaired parts, and the standards of 100%UT, 100%MT and Grade I were implemented, and the test results were qualified.

5. Conclusion

Analyzing the causes of defects is the premise of making a repair plan. Through the inspection case of the desulfurization reactor repair, it can be summarized from two aspects:

(1) Welding: During the welding of 15CrMoR(H) steel, controlling the hydrogen content in the welded joint is one of the important measures to control the cold crack of 15CrMoR(H) steel after welding. This requires that the matching welding materials should be selected to ensure the

chemical composition of the welding seam, the mechanical properties of the welding joint, especially the impact toughness at -10°C . The specific technological measures should be preheating before welding, controlling the interlayer temperature during welding, slowly cooling after welding and reasonable heat treatment. ^[6]

(2) Use management: The user should establish a scientific and reasonable management system, implement the management requirements of daily maintenance and inspection, strictly implement the national regulations on annual inspection and regular inspection of pressure vessels, find hidden dangers and defects in time, nip in the bud, and ensure the safety of equipment use; At the same time, the process of major maintenance of pressure vessels must be supervised and inspected by special equipment inspection and testing institutions with corresponding qualifications, and pressure vessels that have not passed the supervision and inspection shall not be put into use. ^[1]

Acknowledgements

This paper is supported by the Scientific Research Project of Shanghai Institute of Special Equipment Inspection and Technical Research, Project No.2024-05Y and 2024-17Q.

References

- [1] TSG 21-2016 Supervision Regulation on Safety Technology for Stationary Pressure Vessel [S], General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, 2016.
- [2] Conde, A., De Damborenea, J. J., Lopez-Escobar, J. M., et al. Slow strain rate technique for studying hydrogen induced cracking in 34CrMo4 high strength steel [J]. *International journal of hydrogen energy*, 2021, 46(70):34970-34982. DOI:10.1016/j.ijhydene.2021.08.026.
- [3] Li Xiaoyang, Wu Mingyao, Jing Wong, et al. Stress corrosion comprehensive performance evaluation of improved 15 CrMoR (H) material in hydrogen sulfide environment [J]. *Journal of Beijing University of Technology*, 2015(1):142-148. <https://d.wanfangdata.com.cn/periodical/ChlQZXJpb2RpY2FsQ0hJTmV3UzIwMjMxMjI2EhFiamd5ZHh4YjIwMTUwMTAyMhoIbHM1cmJ6Z2o%3D>
- [4] Tang Lina. 15CrMoR steel plate welding technology research [J]. *China Chemical Equipment*, 2016(4):39-41, 20. <https://d.wanfangdata.com.cn/periodical/zghgzb201604009>
- [5] Su Haiqing, Han Shuguang. Welding technology of 15CrMoR steel [J]. *Welding technology*, 2006, 35(5):63-64. <https://d.wanfangdata.com.cn/periodical/hanjiejs200605027>
- [6] Wang Shishan, Bai Jianbin, Li Wei, et al. Development of welding materials for 15CrMoR (H) steel and research on the properties of welded joints [J]. *Electric welding machine*, 2021, 51 (10): 107-113. <https://d.wanfangdata.com.cn/periodic/chloqdata>.
- [7] Peral, L. B., Zafra, A., Belzunce, J., et al. Effects of hydrogen on the fracture toughness of CrMo and CrMoV steels quenched and tempered at different temperatures [J]. *International journal of hydrogen energy*, 2019, 44(7):3953-3965. DOI:10.1016/j.ijhydene.2018.12.084.