Welding procedure Research of Niobium Heat Exchanger

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Abstract: The weldability of R04200 niobium tube-to-tubesheet is analyzed. The macroscopic examination, penetration testing, hydrostatic testing and metallographic examination are tested by the method of GTAW. The results show that specific welding structures with He-Ar mixed gas as shielding gas can improve the arc stiffness, thermal efficiency and penetration. It expresses the great significance of formulating the welding methods guidance of niobium pressure vessels.

1. Property research of niobium tube-to-tubesheet

A pressure vessels order for nitric acid condenser have been received by a company in Shanghai. R04200 niobium tube and 16MnⅡ+ R04200 niobium composite materials are widely used in design of the heat exchanger tube side. R04200 niobium tube is ASTM B394 material (equivalent to Nb1 according to GB/T 8183-2007 in China), R04200 niobium plate in the composite materials is ASTM B393 material (equivalent to Nb1 according to GB/T 3630-2017 in China). The company intends to conduct welding procedure qualification for gas tungsten arc welding (GTAW) before product manufacturing process.

Niobium is a refractory rare metal with high density and low expansion coefficient, silver gray luster, and high-temperature strength. Niobium and niobium alloy have high specific strength, good plasticity, and can be made into thin plates and parts with complex shapes$^{[1]}$. Niobium has excellent corrosion resistance in many corrosive environments. Its corrosion resistance performance is close to tantalum, but its material cost is much lower than tantalum. Therefore, niobium and its alloys are widely used as corrosion resistant materials in the equipment of hydrochloric acid, nitric acid, sulfuric acid, chromic acid, salt and liquid metal, such as condensers in nitric acid industry, composite lining containers in sulfuric acid industry$^{[2]}$, and heat exchangers with strong corrosive resistance in the pharmaceutical industry$^{[3]}$. The niobium materials are expensive, and so its application forms are mainly composite plate and lining. In order to reduce the cost, the thickness of niobium layer is usually designed to be as thin as possible. Composite plates or lining welding is very difficult, because the melting point of niobium material and steel is very different: the melting point of niobium material is 2468°C, the melting point of steel is 1400°C. Niobium metal often is not melting when welding, the steel underneath has become the molten iron. Therefore, niobium plate is often designed to niobium lining pressure vessel and niobium heat exchanger in actual production, and niobium lining plate can be connected by niobium screw, or brazing. R04200 niobium material has stable performance at room temperature, and when heated, it can be combined directly with non-metallic elements.
Niobium tube-to-tubesheet welding usually adopts vacuum electron beam welding or GTAW. According to the welding equipment conditions of the company, GTAW method is adopted. The method of GTAW has many advantages: the molten metal has less contact with air, relatively fewer pores and less heat input, etc. However, the cooling speed of niobium weld joint is low, which will reduce the ductility of the weld seam and lead to welding cracks. There is no relevant standard for niobium equipment in China at present, so the welding procedure test shall be qualified to meet the standard and design requirements according to the code of TSG 21-2016.

2. Welding procedure conditions
The size of niobium tubes ASTM B394 R04200 used in nitric acid condenser is O.D.19.25 mm ×1.5 mm, and the thickness of the tubesheet 16Mn II + ASTM B393 R04200 is 45±2 mm. The tubes extend the tubesheet 1.5mm. The size of the tube-to-tubesheet welding sample is the same as the actual product, which can cover the Nb1 tube with thickness of 1.275~1.725 mm and nominal diameter greater than or equal to 16.3625 mm in welding procedure qualification. After GTAW process is finished, the results of penetration test, metallographic examination and thickness measurement of the fillet weld are verified. The welding structure picture of the tube-to-tubesheet is shown in Fig.1.

2.1 Groove form
The welding groove type of niobium tube-to-tubesheet is mainly determined by joint position, plate thickness, welding method and corrosion resistance requirements. It is difficult to protect the back of the niobium tube-to-tubesheet in the welding process, so the fixture of inert gas protection or special procedure should be adopted to ensure that the welding high temperature zone is not oxidized. The method of expanding of the tube before welding is adopted to enhance the tube-to-tubesheet heat transfer, facilitate the weld forming and prevent the weld back from oxidation. The first layer adopts self-fusion welding without welding wire to form a good molten pool. The sample groove and alignment used in this welding procedure are shown in Fig.2.
2.2 Chemical composition and mechanical properties of niobium material

The chemical composition of the R04200 niobium tubes and plate used in the welding test are shown in Tab.1, and the mechanical properties of niobium tubes and plate are shown in Tab.2.

Tab.1 The chemical composition of the niobium tubes and plate

| Elements Material | Nb | Fe | Si | Ni | W | Mo | Ti | Ta | O  | C  | H  | N  |
|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|
| ASTM B394 R04200 margin | 0.004 | 0.004 | 0.005 | 0.020 | 0.009 | 0.015 | 0.1 | 0.014 | 0.008 | 0.01 | 0.01 |
| ASTM B393 R04200 margin | 0.004 | 0.003 | 0.002 | 0.018 | 0.004 | 0.002 | 0.07 | 0.015 | 0.004 | 0.01 | 0.008 |

H, O, N and other gas may be absorbed by R04200 niobium material from the environment at high temperatures and formed brittle compounds. A small amount of gas impurities can significantly affect the mechanical properties and corrosion resistance. Thus, the niobium material used for welding should be of high purity, and the content of impurities such as H, O, N and other impurity should be strictly controlled in welding material and welding process. Before welding, welding grooves and 30 mm area on the grooves should be mechanical cleaned strictly, degreasing processed. The scale, oil, and fibers on the surface should be erased carefully through acetone to ensure the welding material and the surface of welding grooves clean[4].

Tab.2 mechanical properties of the niobium materials

| Materials                  | Mechanical properties |
|----------------------------|-----------------------|
|                           | $R_{0.2}$ (MPa) | $R_m$ (MPa) | $\delta$ (%) |
| ASTM B393 R04200 plate    | 228                  | 345         | 38           |
| ASTM B394 R04200 tubes    | 264                  | 368         | 41           |

When the niobium material is welded, the cooling rate of niobium material is low, the ductility of weld seam decreases, and the tendency of heating crack is increased. Therefore, the grain size of the niobium material shall be taken into account in the welding test, and fine grains with size less than or equal to ASTM grade 5 should be adopted. The grain size of niobium material in the welding test is grade 3.

2.3 Selection of welding materials

In the GTAW procedure, ASTM B392 R04200 niobium wire with a diameter of 1.2mm is used for filler metal. The grain size of weld seam and heat-affected zone can be refined by using pulsed current inert gas welding with tungsten electrode transverse oscillation, which improve the plasticity of welded joint significantly and avoid excessive hardness.

2.4 Welding procedure parameters

The GTAW welding procedure of R04200 niobium material usually adopts small tungsten electrode diameter and high energy density. In order to test the different welding methods on the welding joint quality of niobium tube-to-tubesheet, the welding process parameters were used for the welding test as shown in Tab.3. The Ar gas with purity of $\geq99.99\%$ and the mixed gas with Ar purity of 70% + He purity of 30% were used for the protective gas respectively.

| Sample No. | Polarity of power | Current (A) | Voltage (V) | Welding speed (cm/min) | Tungsten electrode diameter (mm) | Groove angle | Shielding gas          |
|------------|-------------------|-------------|-------------|------------------------|---------------------------------|--------------|------------------------|
| 1#         | DCEN              | 110 – 130   | 10 – 12     | 24 – 28                | 4Φ.2.4                         | 30°          | $\geq99.99\%$ Ar      |
| 2#         | DCEN              | 110 – 130   | 10 – 12     | 24 – 28                | 4Φ.2.4                         | 30°          | 70% Ar+30% He         |
Due to the welding characteristics of niobium material, the welding site should be an independent area, and the welding environment should be clean to prevent smoke, oil and wind disturbance. During welding, measures should be taken to ensure that the heat transfer conditions of the tubes and tubesheet are close, and the welding arc position should be controlled. Copper rods should be placed in the tubes during welding to accelerate cooling of the niobium tubes and prevent oxidation of the niobium tubes. In addition, the welding area should be strictly protected during post-welding cooling to ensure corrosion resistance of the weld joints.

3. Test results and analysis

3.1 macroscopic examination

The above welding methods and procedures are used to weld the niobium tube-to-tubesheet. The weld joint is beautifully formed with silver-white surface and no oxidation characteristic, as shown in Fig.3 and Fig.4. There is no crack, no pore by 100% PT in the weld seams, which satisfies level I of NB/T47013.5-2015. According to NB/T47014-2014 ‘Welding Procedure Qualification for Pressure Equipment’, 1# and 2# weld joints are examined in profile and the welding foot heights H of the weld seams are measured. The results are shown in Tab.4. The welding foot height of 2# test sample is higher than 1# test sample, and the welding quality of 2# test sample is better than 1# test sample.

| Sample No. | 1# | 2# |
|------------|----|----|
| Welding foot height H (mm) | 2.719 | 3.407 |

3.2 Helium leakage test and hydrostatic test

The helium leakage tests are carried out on the above weld joints to investigate the compactness of the weld joints. The test gas used in the helium leakage tests is 0.8MPa nitrogen gas + 0.2 MPa mixed gas (60% argon gas +40% helium gas), and the test results are shown in Tab.5. The helium leakage tests shows that the helium leakage of 2# sample is lower than 1# sample.

The hydrostatic test is carried out on the above weld joints. The test shows that 1# and 2# weld joints have no leakage, no deformation and no sound when the test pressure is 4MPa and the pressure is maintained for half an hour. 1# and 2# weld joints have no leakage and no sound, but the heat exchanger tubes began to be deformed when the test pressure is 5MPa and the pressure is maintained for 20 min.

| Sample No. | 1# | 2# |
|------------|----|----|
| Leakage rate (10^-9 Pa·m³·s⁻¹) | 1.0 | 0.8 |
3.3 Metallographic examination

The welding process can directly affect the macrostructures and microstructures of the weld metal and the heat-affected zone, as well as the welding defects and property of the welded joints. The microstructure and welding defects of the welded joints can be analyzed by the metallographic examination of the welded joints. After the cross section of the weld samples are polished, both the weld microstructures of R04200 niobium tube-to-tubesheet weld samples by GTAW have no obvious defects, such as cracks, incomplete welding, and no fusion, as shown in Fig.3 and Fig.4. The samples are eroded by the aqua regia solution and magnified 200 times for metallographic examination. It shows that the grain of the weld seams microstructure are obviously grown, and no microcracks and other defects were found in the weld joints, as shown in Fig.5 and Fig.6.

4. Conclusions

Based on the above tests, the analysis conclusions are summarized as follows:

1) Before welding niobium heat exchanger tube-to-tubesheet, it is very important to protect the base metal and clean the surface. During the welding process, it is very important to use inert gas protection and cooling copper rods to prevent oxidation of weld seam and heat-affected zone.

2) In the structural design of welding joints, the use of groove welding is convenient to niobium tube-to-tubesheet welding with high melting point and high thermal conductivity. The method of expanding of the tube before welding is beneficial to weld forming and prevent back oxidation of the weld joints.

3) When GTAW procedures are selected, mixed gas of argon plus a certain amount of helium as protective gas can improve arc stiffness, arc thermal efficiency and increase the weld foot height. The welding quality by GTAW with mixed gas is better than pure argon.

In the manufacture process of R04200 niobium heat exchanger with tube size of O.D.19.25 mm ×1.5 mm, GTAW procedure as shown in Tab.3 is adopted. The outcome of heat exchanger inspection and performance of hydrostatic test can satisfy the design requirements. The test results show that proper structure design, reasonable procedure parameters and effective welding protection measures are the key factors to ensure the welding quality of the niobium heat exchanger tube-to-tubesheet. It has the great significance of the successful welding procedure qualification to guide the welding procedures and actual manufacture of niobium heat exchangers.

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