Welding procedure research of R04200 niobium plates

Jiang Chengjun\textsuperscript{1*}, Meng Jin\textsuperscript{2b}, Zhang Xiaoli\textsuperscript{3c}, Xue Xiaolong\textsuperscript{1d}

\textsuperscript{1}Shanghai Institute of Special Equipment Inspection & Technical Research, Putuo, Shanghai, China
\textsuperscript{2}Shanghai Space Propulsion Technology Research Institute, Minhang, Shanghai, China
\textsuperscript{3}Shanghai Morimatsu Pressure Vessel Co., Ltd, Pu Dong, Shanghai, China
\textsuperscript{b}email: yhjbetter@126.com, \textsuperscript{c}email: zhangxiaoli@morimatsu.cn, \textsuperscript{d}email: xuexl@ssei.cn
\textsuperscript{*}Corresponding author’s e-mail: jiangcj@ssei.cn

Abstract: The weldability of R04200 niobium plates is analyzed. The mechanical property, bending property and corrosion resistance are tested by the butt welding procedure of GTAW. Test results show that butt joints by the welding procedure perform good property, and the corrosion resistance microstructure of the welding joint is normal. The success of the procedure qualification test is of great help to the standard formulation of the niobium pressure vessels.

1. Welding property of niobium pressure vessels

A pressure vessels order for nitric acid concentration system have been received by a company in Shanghai, including niobium vessels such as acid vaporizers and niobium tube heat exchangers. R04200 niobium sheet has been used in design of these pressure vessels recently. The cost of niobium nitric acid condenser is high and the one-time investment is large, but its service life is long, so the annual investment cost is actually economical. In addition, the use of niobium nitric acid condensers during the entire operation of the equipment can avoid the maintenance, leak detection and shutdown caused by frequent accidents, which will greatly improve the safety and reliability of the operation and reduce the operation cost.

R04200 niobium sheet is according to ASTM B393 (equal to Nb1 according to GB/T 3630-2017 in China). It belongs to reactor grade unalloyed niobium. Niobium belongs to refractory metal, and has silver gray luster, low expansion coefficient, and high strength in high-temperature environment. Niobium and niobium alloy have high specific strength, good plasticity, and can be made into thin plates and parts with complex shapes. 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\textsuperscript{[1]}. Therefore, niobium and its alloys are often used as corrosion resistant materials in the equipment of hydrochloric acid, nitric acid, sulfuric acid, salt and liquid metal, such as condensers in the nitric acid industry, composite lining containers\textsuperscript{[2]}, and heat exchangers with strong corrosive resistance in the pharmaceutical industry\textsuperscript{[3]}.

The welding heat source with high energy density and thermal conductive rods should be used, because niobium is a refractory metal with high thermal conductivity\textsuperscript{[4]}. R04200 niobium plate welding usually adopts methods of gas tungsten arc welding (GTAW) or vacuum electron beam
welding or plasma arc welding (PAW). According to the manufacture conditions of the company, GTAW method is adopted. There is no manufacture standard for niobium pressure equipment in China now, so the company should conduct weldability test and welding procedure qualification for the niobium sheet before product manufacturing process according to Chinese code.

2. Welding test conditions

2.1. Test plate material
The thickness of niobium plate is 3mm for this welding test. The welding procedure qualification of NB1-class plate is covered the thickness of weld joint not more than 6mm, which is enough in the nitric acid pressure vessels. The testing niobium sheets are welded by GTAW, and the welding quality, mechanical properties and corrosion resistance performance are tested and analyzed. The welding R04200 niobium sheet sample is shown in Fig.1.

![Fig.1 the welding R04200 niobium sheet sample](image)

The chemical composition and mechanical properties of ASTM B393 R04200 niobium plate used in the test are shown in Tab.1 and Tab.2.

| Tab.1 The chemical composition of the test plate |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Elements       | Nb  | Fe  | Si  | W   | Ni  | Ti  | Mo  | Ta  | H   | O   | C   | N   |
| Material       | R04200 margin | 0.004 | 0.003 | 0.018 | 0.002 | 0.002 | 0.004 | 0.07 | 0.01 | 0.015 | 0.004 | 0.008 |

When welding, gas elements of H, O, N may be absorbed by R04200 niobium plate from the environment at high temperatures. They can be formed as brittle compounds with the material metals, which have a huge impact on the mechanical properties and corrosion resistance of the weld joint. Thus, it is not only ensure that the material composition and performance meet relevant quality standards, the test sheet should be strictly cleaned before welding and protected during welding. Before welding, the surfaces of the welding test sheet should be cleaned by mechanical grinding and erased carefully by acetone within 50mm of the grooves. The welding area of the test plate should be cleaned by a silk cloth without fluff, and the welding test plate should be dry in a clean environment\(^\text{[5]}\).

| Tab.2 mechanical properties of the test plate |
|----------------|----------------|----------------|
| Material       | Mechanical properties |
|                 | R\(_{P0.2}\) (MPa) | R\(_{m}\) (MPa) | A (%) |
| ASTM B393 R04200 niobium plate | 237 | 365 | 38 |

2.2. Welding groove
The welding groove type of niobium sheets is mainly determined by joint position, sheet thickness, welding method and requirements of corrosion resistance. For niobium sheets with a thickness of less than 4mm, V-shaped groove with small angle should be selected as far as possible in butt welding.
design to reduce consumption of welding materials and welding deformation\[6\]. The welding procedure of drag cover and pad protection with gas lens is chosen in GTAW. The sample assembled and aligned in this welding test is shown in Fig.2.

![Fig.2 assembled and aligned form of the welding test sample](image)

2.3. Welding materials and welding machine
ASTM B392 R04200 niobium wires with a diameter of 1.6mm are used for welding materials in the GTAW process. The physical and mechanical properties of niobium wire are related to the purity of the metal and the original condition of the metal, which depends on the content of impurities in the wires, pressure processing conditions and heat treatment conditions. Therefore, the qualified welding wires are the primary guarantee of the welding materials.

Welding machine with the functions of automatic tracking of arc pressure feedback, air flow control, current control, welding torch rotation control, wires feed control, yaw control of the torch head and arc length control and partition setting control programs and other functions.

2.4. Welding procedure
GTAW welding procedure parameters of R04200 niobium sheet are shown in Tab.3. It is prefer to the welding process of small tungsten electrode diameter, small heat input and multi-pass welding when GTAW process of niobium sheet is used. For type V-shaped groove with small angle, DCEN is preferred, and small convex weld bead is preferred.

| Welding procedure | Weld layers | Current type & polarity | Voltage (V) | Current (A) | Travel speed cm/min | Tungsten electrode diameter (mm) | Argon flow rates (L/min) | Main burner | Additional protection |
|-------------------|-------------|-------------------------|-------------|-------------|---------------------|---------------------------------|---------------------------|-------------|----------------------|
| manual GTAW       | 1           | DCEN                    | 9~12        | 120~150     | 24~28               | Φ1.6                           | 10~15                      | 20~30       |                      |
|                   | 2           | DCEN                    | 9~12        | 120~150     | 24~28               | Φ1.6                           | 10~15                      | 20~30       |                      |

No preheating, interlayer-temperature≤100℃

It is not only necessary to adopt strict technological measurements in cutting, groove processing, forming and other procedures, but also have special requirements of the welding environment, pre-welding cleaning and welding protection due to the welding characteristics of niobium materials\[5\]. At first, welding operation should be carried out in a clean and dust-free environment. Secondly, The welding shielding gas adopts high purity argon with purity of 99.995% or more, low water content and dew point ≤ -50℃. The most important technology measure in the welding procedure of gas protected niobium is to strengthen the protection of the welding high temperature zone. A large porcelain mouth is adopted, and a drag cover is used to protect the high-temperature part of the joint where the welding joint temperature is higher than 350℃. Copper wire net is added in the drag cover to enhance the effect of gas screen. During welding, air is supplied in advance and stopped after delay to ensure that the high temperature zone is always under the protection of inert gas during welding.
2.5. Welding process and post-welding heat treatment
A skilled welder conduct the welding operation according to the procedure in Tab.3. The measures, such as cleaning before welding, wearing clean labor protection products, strengthening the inert gas protection are strictly implemented. Then the niobium welding samples are machined into 2 pieces for simulated post-welding heat treatment reduce the risk of corrosion failure in service according to the manufacturing heat treatment status of all bearing parts. The welding sample is divided into two types: 1# sample maintain the as-welded state as same as vessel shells, 2# sample undergo vacuum annealing treatment at 1200°C as same as vessel heads, and the holding time is 1h.

3. Test and results analysis
The following tests are carried out on these niobium welding samples by referring to the standard of NB/T 47014-2011 according to the design requirements.

3.1. Mechanical properties test of the weld joint
The test results of the weld samples on the mechanical properties are shown in Tab.4.

Tab.4 mechanical properties of the weld samples

| Samples NO. | Nondestructive testing (RT+PT) | Visual inspection | Tensile strength Rm MPa (The fracture is located in the heat-affected area) | Face bend and root bend (4 groups) D=40mm (180°) |
|-------------|--------------------------------|------------------|-----------------------------------------------------------------|-----------------------------------------------|
| 1#          | qualified                      | good, weld joint is silver gray | 297.6, 332.4                                                   | intact, no cracks observed                    |
| 2#          | qualified                      | good, weld joint is silver gray | 281.3, 312.1                                                   | intact, no cracks observed                    |

The mechanical and bending properties of 1# and 2# samples can satisfy NB/T 47014-2011 ‘Welding Procedure Qualification for Pressure Equipment’ in Tab.4. The fracture strength of the tensile samples is not high, but their fracture sites are consistent in the heat-affected zone near the edge of the weld seams. The structure of the heat-affected zone is the large recrystallization structure, which will lead to the crack and fracture under the function of tensile stress. The hardness test results are shown in Tab.5. The hardness values of 1# and 2# samples have little difference at the same site. On the whole, the hardness value of base metal < heat-affected zone < weld seam, but there is no large gap. There is no obvious microstructure embrittlement and degradation occurred in the heat-affected area of the two samples, which is favorable to the whole microstructure and mechanical properties.

Tab.5 hardness test result of the weld joints

| Samples NO. | Weld spot position | Hardness (HV0.2/30) |
|-------------|--------------------|---------------------|
|              |                    | Base metal | Heat-affected zone | Weld seam |
| 1#          | upper surface      | 67, 70, 66 | 76, 77, 75         | 90, 95, 92 |
|             | reverse surface    | 68, 65, 69 | 78, 82, 81         | 93, 82, 89 |
| 2#          | upper surface      | 62, 63, 66 | 74, 71, 69         | 87, 84, 91 |
|             | reverse surface    | 59, 64, 63 | 69, 66, 67         | 77, 76, 82 |

3.2. Metallographic examination
The welding procedure can affect directly the microstructures of the weld metal and the heat-affected
zone, as well as the welding defects and the performance of the weld joints. It can be observed that the grains of the weld seam are growing up significantly in the microstructure pictures, which had the typical characteristics of the welding pool, as shown in Fig.3 (a) and (b). The welding pool shape had nothing to do with the crystallization direction, and the bottom of the weld seam had small bumps. The dendrite branching were occurred on the edge of the weld pool. The dendrite growth direction of the weld zone is mainly along the direction of weld seam, which is accordance with the principle of metallography solidification. No holes, cracks and other defects in the weld zone are observed. The heat-affected zones on both sides of the weld seam were recrystallized structures. According to the size of the recrystallized zone, the width of the heat-affected zones on both sides was about 5-6 mm. The grain size near the weld zone reached 0.5 mm and the closer to the weld zone, the larger the grain size was, as shown in Fig.3 (c) ~ (f). The forming and microstructures of 1# and 2# samples were good.

3.3 Intercrystalline corrosion test

The corrosion resistance of niobium material lies in the formation of a dense oxide film on its metal surface, which has high dielectric constant and high breakdown voltage. Therefore, the performance of chemical corrosion resistance does not need to be considered. What needs to be considered is the intergranular corrosion resistance of R04200 niobium weld joints because the weld joints are in contact with the corrosive media. Intercrystalline corrosion test is required to evaluate the corrosion
resistance of the weld joints. According to design requirements, 1# and 2# samples were corroded in boiling nitric acid solution for 120h after they were grinded and polished. Referring to the method A of GB/T 15260-2016, the intercrystalline corrosion tests of 1# and 2# samples were carried out. The test results showed that only an opening defect of less than 1 mm length was found on the outer surface of 1# sample after bending, but the samples all qualified the corrosion test, as shown in Tab.6.

| Niobium sheet | Sample No. | Test procedure | Heart bending diameter | Angle of bend | Results                          |
|---------------|------------|----------------|------------------------|---------------|----------------------------------|
| ASTM B392 R04200 | 1#         | referring to GB/T 15260-20 | 8mm | 180° | qualified (with a 1mm opening defect) |
|               | 2#         |                | 8mm | 180° | qualified                        |

4. Conclusion
In this paper, the weldability of R04200 niobium plate by GTAW procedure on the butt weld joints is analyzed. The forming quality, mechanical properties and corrosion resistance of the weld joint are analyzed by performance tests of R04200 niobium plate after the post weld heat treatment of as-weld and annealing states. The results show that the GTAW procedure can get the butt joint with good performance, the metallographic structures of the weld joints are normal, and the corrosion resistance meet the design requirements.

In the manufacture process of R04200 niobium liner pressure vessels with thickness of 2mm, the outcome of GTAW procedure as shown in Tab.3 can satisfy the design requirements. The test and production practice inspection show that the welding procedure of GTAW is feasible to the welding property and structure of R04200 niobium plates. The welding quality, bearing capacity and corrosion resistance can fully meet the quality and performance requirements of pressure vessel in nitric acid concentration system. The success of the procedure qualification test is of great help to the standard formulation of the niobium pressure vessels.

Acknowledgements
This paper is belonged to Science and Technology Project of Shanghai Administration for Market Regulation (2019-25). The completion of the paper is attributed to the team's support and encouragement.

References
[1] Richard C. Sutherlin, Ronald A. Graham. Corrosion of Niobium and Niobium Alloys[M]. Materials Press. USA, 2005: 325-336.
[2] Bayer Corp, Renner M. Niobium for Hot Concentrated Nitric Acid: Material Selection and Field Experiences with Nb Shell & Tube Heat Exchangers[J]. Reactive Metals in Corrosive Applications Conference Proceedings. Wah Chang, 1999: 25-32.
[3] Stark H C, website, http://www.hcstark.com/main26.html, June 22, 2001.
[4] Corscia, Mike. Tantalum and Niobium for the Pharmaceutical Industry[J]. Tantalum Press Monitor. USA, 1996: 192-206.
[5] Li S.R., Wang X.H., Ding Q.F., et al. Welding handbook[M]. Beijing: China Machine Press, 2008.
[6] Huang Boyun, Li Chenggong. Welding manual for nonferrous materials[M]. Beijing: Chemical Industry Press, 2009: 200-215.