Welding procedure research of R60702 zirconium pressure vessels

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Abstract In order to improve efficiency and reduce costs, the new PAW plus GTAW method for R60702 zirconium plates used in acetic acid production unit is analyzed. The microstructure and mechanical properties are tested by PAW procedure. Through the test analysis and the measured data in the practical application, the butt joint welded by the PAW procedure can satisfy the standard requirements of mechanical properties, corrosion resistance. The success of the welding procedure qualification shows that the new PAW plus GTAW method has great advantages over the traditional GTAW method.

1. Welding property of zirconium pressure vessels

A pressure vessels order for acetic acid production unit was received by a company in Shanghai, including reaction distillation tower, extractor tower reboiler and finished tower reboiler. R60702 zirconium plates were widely used in design of these pressure vessels. In order to improve efficiency and reduce costs, the new welding method of plasma arc welding (PAW) plus gas tungsten arc welding (GTAW) was to replace the original GTAW welding process of the zirconium plate in the company, because the order contained of too many containers and the zirconium plates were thick. Since the original GTAW procedure can cover the thickness of the welding cover by GTAW, only the new PAW method can be used for welding procedure qualification according to the code and standards.

R60702 zirconium plate is ASME SB551 unalloyed zirconium (industrial pure zirconium) material, which is equivalent to Zr-3 in standard of NB/T47011-2010 in China\textsuperscript{[1]}. Zirconium is a rare precious metal with high melting point and has excellent corrosion resistance in most organic acids, inorganic acids, strong bases and some molten salts. Therefore, zirconium is suitable for pressure vessels with special corrosion resistance requirements. With the continuous development of material science and manufacture technology, zirconium is increasingly used in strong corrosion equipment, such as acetic acid, nitric acid, hydrochloric acid, urea, hydrogen peroxide, polyformaldehyde and chlorinated polyethylene\textsuperscript{[2]}. Because the manufacture of zirconium materials is difficult, and there are very few manufacturers in the world, so the price is expensive and the ordering period is very long. Therefore, it is of great significance to improve the welding method and save plate materials and welding materials from the perspective of economy.

Zirconium and zirconium alloys have good weldability and can be welded by fusion welding, brazing welding, solid state welding and other methods\textsuperscript{[3]}. There are many advantages of Zirconium as welding structural material: the thermal expansion coefficient of zirconium is small, so the welding deformation is small; the elastic modulus of zirconium is small, so the welding residual stress is small;
Zirconium is less sensitive to welding cracks. But zirconium is a very reactive metal: zirconium has a strong affinity for hydrogen, oxygen, and nitrogen in the ambient environment. Zirconium strongly absorbs hydrogen at 315–1000°C, absorbs oxygen at 400°C and more, absorbs nitrogen at 800°C and more. When hydrogen, oxygen, nitrogen and zirconium are absorbed to form brittle compounds, not only the plasticity and toughness of zirconium decrease significantly, but also the corrosion resistance of zirconium decreases sharply. Oxygen has a great influence on plasticity and toughness of the weld joint, while nitrogen has a great influence on corrosion resistance[4]. Therefore, the heat affected zone, weld metal and back side of zirconium should be protected by inert gas in the whole welding time.

PAW is a fusion welding method using high energy density beam of plasma arc as welding heat source. PAW has the characteristics of energy concentration, high productivity, fast welding speed, small stress deformation and stable electric arc, etc. It is especially suitable for welding all kinds of refractory, easy to oxidize and strong heat sensitive metal materials. Compared with GTAW method, the advantage of PAW is that it need little or no groove pre-processing before butt welding, the overall operation time is reduced, and the time of material cooling down is far less[5]. In the welding work of zirconium pressure vessels, if the manual GTAW method is used, the welding efficiency is very low and the time is too long. In addition, the thermal conductivity of zirconium material is poor, so the amount of used shielding gas is very large and the cost is higher. If the PAW method is adopted, the production efficiency can be improved, the welding time can be saved, and also the cost of using the shielding gas can be greatly saved.

2. Welding procedure test of R60702 zirconium pressure vessels

2.1. Specification of R60702 zirconium test plate
The shell plate thicknesses of the R60702 zirconium pressure vessel in the acetic acid production unit are two specifications: 8.5mm and 12mm. The following manufacturing processes are planned to be adopted: 8.5mm zirconium plate is welded by PAW without backing plate on the reverse side to forming the reverse side with good quality; 12mm zirconium plate is welded by PAW in the first weld layer, then covering welded by GTAW. In order to qualify these thicknesses of P61 type zirconium plate welding procedure, the zirconium plate of 10mm is selected in this test. This test niobium plate is welded by PAW, and the mechanical properties, bending property and corrosion resistance are tested and verified, as shown in Fig.1.

Fig.1 the R60702 zirconium plate for welding

2.2. Material test report of zirconium materials
The chemical compositions of the zirconium test plate used in the test are conforming to ASME SB551 R60702, as shown in Tab.1. The mechanical properties of the zirconium plate are shown in Tab.2. There is no welding wire in the planned PAW procedure. PAW without welding filler material can keep the weld metal pure and is less prone to produce defects like slag inclusions.
Tab.1 The chemical composition of the R60702 zirconium plate

| Elements | Zr+Hf | Hf   | Fe+Cr | H     | N     | C     | O     |
|----------|-------|------|-------|-------|-------|-------|-------|
| content  | 99.3  | 3.0  | 0.12  | 0.002 | 0.02  | 0.03  | 0.11  |

Tab.2 mechanical properties of the R60702 zirconium plate

| Material                  | Mechanical properties |
|---------------------------|-----------------------|
|                          | R_{0.2} (MPa) | R_m (MPa) | δ (%) | Bend test |
| R60702 zirconium plate    | 228             | 395        | 31    | qualified |

In the R60702 welding process, welding work should be carried out in a clean special site to strictly controlling the pollution of Fe ion and the environment. The high purity inert gases (purity \( \geq 99.998\% \)) should be used to protect the welding area. At the same time, the protection range of inert gases should be reasonably expanded without affecting the welding operation. When the welding heated area is above 250°C, it should be protected by inert gases and the supply flow of inert gases should be increased to reject the influence of light element gases (O, H, N) on the crystallization of the weld seam. It can reduce the residence time of the weld seam at high temperature, and control the growth tendency of crystalline grains in the weld seam and heat-affected zone\(^6\).

2.3. Alignment and groove form

The zirconium plate welding by PAW generally only need to machine a slanting guide angle with depth of 2~3mm, opening angle of 80°±5°. Welding test plate should be aligned and the gap should be small enough with the actual error should be controlled in 0~0.5mm. If there is a lot of metal leakage at the back side after welding, a small groove can be added on the back. Alignment and groove form are shown in Fig.2.

![Fig.2 Groove form of the R60702 welding test sample](image_url)

The groove should be made by mechanical processing, such as turning, milling, planing or grinding, which should avoid metal overheating. The groove surface shall be smooth and free of cracks, burrs, bumps or overlaps. When grinding, the clean grinding wheel should be used and the surface should be polished by an austenitic stainless steel wire brush or mechanically to remove any metal particles that may remain on the surface of the groove during grinding. Oil stains and dusts should be clean by acetone at the range of at least 50mm on both sides of the welding groove. The surface should be kept clean and not touched by hands. Welding should be performed immediately after groove cleaning.

2.4. Welding procedure parameters

PAW procedure parameters of R60702 zirconium plates are shown in Tab.3. The ratio of shielding gas and flow adjustment are the key factors in welding process. Through many tests, the best effect is the shielding gas ratio of 40% He gas plus 60% Ar gas (partial pressure ratio), which is changed from the original pure Ar gas. The flow rate should be adjusted in time according to the forming condition of the test welding sample, which generally does not exceed the range of 3~5 L/min defined in Tab.3. The reason for increasing He gas is to enhance the welding penetration. The thicker the plate, the stronger the penetration of the shielding gas is needed. There is no preheating measure, and the interlayer temperature should be not more than 100°C.
Tab.3 PAW technological parameters

| Parameters | Weld layers | Cerium tungsten electrode diameter (mm) | Current type & polarity | Current (A) | Voltage (V) | Travel speed cm/min | Argon flow rates (L/min) main burner Additional protection |
|------------|-------------|----------------------------------------|-------------------------|-------------|-------------|--------------------|----------------------------------------------------------|
| PAW        | 1           | Φ3.0                                   | DCEN                    | 180~220     | 34~36       | 20~30              | 20~25                                                   |
|            |             |                                        |                         |             |             |                    | 50~75                                                    |

3. Test results and analysis

3.1. Performance test of the weld sample

Through the welding procedure test, the R60702 zirconium plate is welded successfully, as shown in Fig.3. The welding seam on the test plate is full and the welding pattern is beautiful. No surface defects were found by visual inspection. The results of weld sample performance test are shown in Tab.4 for this test condition.

![Fig.3 the R60702 zirconium welding test sample](image)

Tab.4 results of the weld sample performance test

| Test items | Nondestructive testing (RT+PT) | Visual inspection | Tensile strength Re MPa | Face bend+ back bend D=50mm (180°) |
|------------|---------------------------------|-------------------|--------------------------|-----------------------------------|
| Results    | Qualified                       | Good, weld metal is silver-white | 397.6, 432.4             | Intact, no cracks observed        |

The mechanical properties and bending property of the R60702 zirconium welding sample can satisfy NB/T 47014-2011‘Welding Procedure Qualification for Pressure Equipment’ in Tab.4. The fracture site of the tensile samples is the heat-affected zone of the welding joint, which is related to the coarse recrystallized microstructure of the heat-affected zone in metallographic examination. Two groups of face bent samples and two groups of back bent samples were taken for 180° bending test. No opening defects were found. The surface hardness of each position on the weld joint was tested. The hardness test results are shown in Tab.5. The hardness value of base metal is less than heat-affected zone, and also less than weld seam, which is in line with the normal hardness distribution of weld joints. In general, the surface hardness of the weld joint reflects the microstructure change of each part of the joint to some extent. Obviously, this sample does not have obvious microstructure deterioration, and the welding quality is good.

Tab.5 hardness test of the welding point

| Test items | Weld spot position | Base metal | Heat-affected zone | Weld seam |
|------------|--------------------|------------|--------------------|-----------|
| Hardness (HV0.2/30) | upper surface | 69, 71, 68 | 78, 78, 75 | 82, 88, 81 |
| | reverse surface | 66, 66, 69 | 74, 80, 82 | 83, 85, 85 |
3.2. Metallographic examination

Metallographic inspection of weld joints is used to check the microstructure of weld seams, heat-affected zones and welding workpieces, and to determine internal defects, etc. Through analyzing metallographic structure of the weld joints, the quantity, grain size and structure state of various substances in the weld metal can be inspected, so as to understand the properties of the weld joints and provide the basis for improving the welding procedure, formulating the heat treatment process specification and selecting the welding material. The cross section of the weld joint is observed by naked eye and 10x magnifying glass. There are no defects found such as incomplete penetrations, slag inclusions, cracks and pores, as shown in Fig.4 (a). The 200-fold microscopic examination of the weld seam and the heat-affected zone on both sides shows that the microstructure of the metallographic seam matrix is a zirconium solid solution, and the grain size of the weld seam microstructure is obviously grown. The heat-affected zone on both sides of the weld seam is the coarse recrystallized structure. No microscopic defects or microstructure defects are found in the heat-affected zone and the weld seam, as shown in Fig.4 (b)–(d).

![Metallographic structures of the welding test sample](image)

3.3. Corrosion test

When weld joints contact with corrosive media, the corrosion phenomenon between grains is called intergranular corrosion. The weld joint will fracture along grain boundaries and almost completely lose strength under the action of external stress when intergranular corrosion occurs. The intergranular corrosion is one of the most dangerous forms of failure for weld joints. In order to evaluate the corrosion resistance performance of R60702 zirconium weld joint, it is necessary to conduct intergranular corrosion test on the weld joints. After the sample is processed and polished, it is immersed in a boiling 98% concentrated nitric acid solution for 120h. The intergranular corrosion tendency test is carried out on the sample according to the design requirements. The test results show that there is no opened defect on the outer surface of the sample after bending, as shown in Tab.6. The performance of the sample’s corrosion resistance is qualified.
### 3.4. Procedures comparison of PAW and GTAW

By comparing the process of PAW and the previous GTAW, it can be concluded that:

1. The weld joint formed appearance of PAW is better than that of GTAW;
2. The used welding materials by PAW are less than those by GTAW. Take zirconium plates with thickness of 12mm as an example: for the traditional X-shaped double-sided groove type, about 2 kg welding wires are consumed in a longitudinal weld seam of 2.4m length, which is equal to 0.83 kg/m. The total length of the butt weld on the whole reaction distillation tower is 83 m (longitudinal seams) plus 147 m (circumferential seams), which is needed 191 kg welding wires. The whole zirconium tower welding by PAW and PAW plus GTAW using procedure shown in Tab.3 only needs one roll wire of 15 kg;
3. The inert shielding gas with high purity is saved by PAW. The total gas flow is about 80L/min by GTAW, and the flow time of the 2.4m longitudinal seam is about 4h, so the total gas consumption is about 19.2 m³. If the 2.4m longitudinal seam is welded by PAW, the total gas flow is 120L/min, and the flow time is about 1h, so the total gas consumption is 7.2 m³, which is saving more than half of the shielding gas;
4. The operation time is saved by PAW. Taking the 2.4m longitudinal seam as an example: the pure welding time by GTAW is about 4h, but that by PAW is about 1h. Therefore, the efficiency of PAW is about 4 times of GTAW.

Although the shell weld seam by PAW is good, there are still some disadvantages:

1. The vertical pairing shells are limited by the number of cylinders, so it may not apply to the procedure of PAW. If the groove condition of horizontal pairing is not allowed, GTAW procedure can be used.
2. Some special weld seams, such as circumferential seams of heads, circumferential weld joints of cone shells, the final closing weld seam, are difficult to ensure accuracy of alignment size. Therefore, GTAW procedure is still relatively reliable for these joints.

### 4. Conclusions

In order to improve the manufacture efficiency and reduce the cost of zirconium pressure vessels, the weldability of R60702 zirconium plate is analyzed in this paper and the new PAW procedure is used to replace the original GTAW procedure. The test sample by PAW procedure is welded and tested, and its advantages and disadvantages were compared with the original GTAW procedure. The test results show that suitable groove design, effective inert-gas protective measures and skilled welding technology are essential conditions to ensure the welding quality by PAW.

In the manufacture of actual pressure vessels in the acetic acid production unit, the R60702 zirconium pressure vessels with 8.5mm thickness are manufactured by the PAW procedure listed above, and the R60702 zirconium pressure vessels with 12mm thickness is manufactured by PAW plus GTAW procedure. They all passed the acceptance. The success of the procedure qualification and completion of the project are of great significance to the manufacture of zirconium pressure vessels.

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