Zirconium has excellent corrosion resistance to acid, alkali and a variety of metal fluids. It has superior corrosion resistance to niobium, titanium and some other metals in certain corrosive mediums, which makes it suitable for corrosive media where titanium is not. [1]

Zirconium has, therefore, found more and more application in modern petroleum and chemical industries. However, zirconium is among the more expensive metals, which means the cost of pressure vessel manufacturing using full-thickness zirconium plate would be extremely high, especially for large scale high temperature and pressure equipment, prohibiting its widespread use.

On the other hand, zirconium-steel composite plate becomes an economically viable material for the manufacturing of such pressure equipment. In this paper, welding technology and inspection characteristics of the core equipment - the reactor used for the synthesis of acetic acid by the method of methanol carbonylation - are briefly introduced. Moreover, some details that should be taken into consideration in the fabrication of the zirconium-steel composite plate equipment are briefly described.

**Technical parameters of the reactor**

The main technical parameters of the reactor are shown in Table 1, while the dimensions of the reactor structure are shown in Figure 1. The main body is made of zirconium-steel composite plate (SA516Gr55 and RB60700). The material and dimensions of the top and bottom spherical vessel head are SR1653+23+4, and the cylinder has dimensions of Ø300×460+(60+4.76) with the stirring part as internal components.

**Welded joint design**

Fusion welding is not suitable between zirconium and steel due to a series of brittle intermetallic compounds that will form in the welded joint. As a highly active metal, zirconium is easily embrittled by impure elements at high temperature, especially nitrogen, oxygen, hydrogen and carbon. Hence, it is difficult to obtain a sound welded joint directly by fusion welding [2]. At present, the zirconium-steel composite plates are widely joined by fusion welding of the steel base layer and the zirconium composite layer respectively, to prevent any mutual fusion between the two layers. Firstly, the steel base layer is welded. After the post-weld inspection, the zirconium composite layer is welded independently.

**Longitudinal and circular welding seam on the backing plate and cover plate**

The welding of zirconium and steel composite plate is prepared as follows. Dual side protection is applied during welding of the longitudinal and circular seam of the composite layer. Firstly, welding is performed on the steel base layer. Afterwards, the welded seam on the base layer is ground until flush with the base layer and an inspection is performed on the welded seam. Sequentially, the zirconium backing plate, which is also the cover layer, is placed, with the bottom surface firmly covering the top surface of the composite layer (in the middle), as shown in Figure 2. Welding on the composite layer and sequential inspection is then performed.

Lastly, the zirconium cover layer is welded. It is worth noting leak detection pipe can be used as the gas flow tunnel for the welding of zirconium cover and composite layer. Also, it can be designed as the leak protection system for the manufacturing of the equipment.

**Welding experiments**

During the manufacturing process of the reactor, five welding methods including manual gas tungsten arc (GTAW), electrode shielded metal arc welding (SMAW), submerged arc welding (SAW), and plasma arc welding are used with consideration of the material, heat input and lateral shrinkage. The base layer is made of SA516Gr55, which is a slow carbon steel that has good weldability. The conventional welding methods and processes are suitable for this steel. However, due to the speciality of the structure and material of the zirconium-steel composite plate, it is an important requirement that the heat input of the base layer during welding, especially for the joint that is adjacent to the composite plate, should not be too high. In the manufacturing process, the welding preparations of the longitudinal and circular welding seams are prepared using beveling machine. The backing GTAW welding pass is initiated from the inner side, following by two or three fill layers using shielded metal arc welding. The remaining layers are filled from the outside using narrow-gap submerged arc welding. With this method, the welding heat input is assured to be low and the cleaning of the root weld pass with gas gouging is not necessary. Moreover, the lamination of the joint is not badly affected.

The welding parameters of the base steel layer are listed in Table 2.
The welding bevels for connecting pipes on the cylinder are machined using a floor type boring and milling machine. The root pass is finished by manual GTAW with subsequent passes being completed using SMAW. The process is not complex. After welding of the base layer, X-ray and ultrasonic inspections are performed on the welding joint. The entire weldment is then transferred into the furnace for heat treatment.

The high temperature during heat treatment reduces the peel strength of the composite plate and the surface of the composite layer gets over-oxidised. With the design and related specification being required, the holding temperature should be low and the holding time should be as short as possible.

Also, the inner should be cleaned before the heat treatment, and at least two layers of titanium-based high temperature coating are necessary on the inner wall. The heat treatment specification for the reactor is 380°C for three hours. **Welding of composite layer.**

The inner composite layer is commonly made of ZR700, R60700, while the backing plate and cover plate are still made of R60702. Compared with R60702, R60700 has the similar welding ability and corrosion resistance but the oxygen content and the strength are slightly lower. It can be directly explosion welded with low carbon steel. The titanium is usually added as the interlayer between R60702 and carbon steel to produce the zirconium-steel composite plate [3]. Zirconium is very active at high temperature and a series of brittle intermetallic compounds will form in the welded joint due to air absorption, especially due to oxygen.

The welded joint will be embrittled. The corrosion resistance and the machining properties will also be affected. Therefore, in order to prevent gas pollution during welding, it is necessary to shield the weld joint using purging devices. Pure argon (>99.99%) is used in the high temperature zone (>400°C) of the weld joint and the weld seam is rapidly cooled. The impure elements, especially carbon, can greatly affect the corrosion resistance of the weld seam. When there is a small amount of carbon (<0.05%), the corrosion resistance will be drastically reduced. Therefore, it is necessary to clean the oil and other contaminants on the surface of the welding part, to prevent contamination [4].

The welding parameters for the zirconium composite layer, cover plate, connecting pipe and cylinder on the reactor are shown in Table 3. The welding quality of the zirconium composite layer is related to the long-term safe operation of the equipment. The welding processes are introduced as per Table 3. While welding between the backing plate and composite layer, welding gaps should be as even as possible and must be between 1.0 and 2.0 mm. If it is smaller than 1.5 mm, it cannot guarantee the design requirements of the welding depth of 2.0 mm. Otherwise the base metal will melt and cause hot cracking in the weld seam. If it is difficult to control the welding gap precisely, it is better to let the welding gap be as small as possible. Meanwhile, a 1.0 mm 45° groove is machined into the backing plate so that the reinforcement of welding between the backing plate and the composite layer is small. This can also ensure welding penetration of 2.0 mm according to the design requirements. For the welding between cover plate and composite layer, there is always misalignment in the longitudinal and circumferential welding seam in the cylinder. Hence the gap between the welding seam of the cover plate and the composite layer is different. When the pair of cover plates is mounted, the gap should be even and as small as possible.

Two welding passes are performed, in which the arc ignition and arc blow out locations are staggered. The first welding pass is performed using a welding wire of Ø0.4 mm. A small amount of filler wire, which assures the full penetration of weld leg, is used. The second welding pass is performed using a welding wire of Ø2.3 mm. The weld fill is normally finished when the size of the weld leg is big enough. Figure 5 shows the welder is operating on the cover plate and composite layer and the forming quality of the weld. It is worth noting that the high-purity argon in the leak detection pipe can replace the air at the back of weldment to prevent contamination. While
For the longitudinal joints of zirconium, the welding difficulty is very difficult. In the production process, two stations are performed. The test pressures are 11.12 MPa and a temperature of 210 °C in an electric furnace with compressed air as a medium after the water pressure and air tightness test. Testing temperature and pressure are shown in Figure 8. As the testing pressure and temperature are reached, the equipment is held in the testing conditions for four hours. If there is no leakage and abnormal deformation, the equipment is qualified.

Nuclear leak detection: Acetic acid, iodomethane and other reaction liquids are strong corrosive media for the reactor. As there is a steel layer barrier, they cannot be observed immediately once they are leaking from a weld. The strong corrosive media can, therefore, cause the corrosion of the steel base very quickly, with the possibility of serious accidents on the pressure vessel occurring.

The fillet welds on the zirconium composite layer have low carrying capacity and the weld quality is difficult to guarantee. Generally only non-destructive testing can be performed on the surface, while it is difficult to detect the flaws by using radiation or ultrasonic. Pressure tests cannot ensure that the abnormal sound during the test. The equipment can then be qualified.

Thermal cycling test: The thermal expansion coefficient of zirconium, which is 5.3×10⁻⁶ per °C, is much lower than that of low carbon steel, which is 11.12×10⁻⁶ per °C. As the temperature of the reactor rises, the zirconium composite layer will bear large tensile thermal stress.

The welds on the zirconium composite layer are mostly overlapped fillet welds with low load carrying capacity. Thermal cycling tests can test the thermal stress-bearing capacity of zirconium composite welds under the non-corrosive media at designated temperature and pressure [6]. The reactor was subjected to a thermal cycle test with a pressure of 3.3 MPa and a temperature of 210 °C in an electric furnace with compressed air as a medium after the water pressure and air tightness test. Testing temperature and pressure are shown in Figure 8. As the testing pressure and temperature are reached, the equipment is held in the testing conditions for four hours. If there is no leakage and abnormal deformation, the equipment is qualified.

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References