ZIRCONIUM EXPLOSION CLAD FOR COST EFFECTIVE PROCESS EQUIPMENT: APPLICATIONS, DESIGN, FABRICATION

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ABSTRACT

Zirconium explosion clad offers cost and performance benefits for chemical process equipment. Seven specific equipment applications are reviewed, including corrosion and operating conditions, unique fabrication concerns, and performance history.   An overview of clad fabrication techniques, including welding, forming, and heat treating is presented. Unique clad manufacturing issues are discussed. Clad specifications and inspection processes are reviewed.

INTRODUCTION

Zirconium's superior corrosion resistance is ideal for a broad range of inorganic and organic chemical environments (Ref 1-3). Today's process industries chose zirconium as the preferred material of construction for a broad range of equipment including tanks, columns, pressure vessels, and heat exchangers.   However, when pressures and/or temperatures and size demand thick plate, the zirconium equipment can become considerably more expensive than units constructed from lower cost, inferior performance alloys or non-metals.   Zirconium clad offers a reliable, cost effective alternative, providing zirconium clad equipment which is cost competitive in comparison with many of the less reliable alternatives.   The explosion cladding process produces a high quality zirconium clad product with proven fabrication and operations performance. Explosion clad, with base metals of both carbon and stainless steel, have been used extensively in process equipment.

ZIRCONIUM CLAD IN PROCESS EQUIPMENT

Advantages of Zirconium Explosion Clad for Process Equipment

- For thick vessels, explosion clad reduces cost. In the current marketplace, zirconium clad typically provides a cost benefit when heat exchanger tubesheets exceed 25 mm thickness and when vessel plates exceed 12mm thickness (dependent upon zirconium thickness.) Figure 1 presents cost comparisons of zirconium clad carbon steel vs solid Zirconium 702.
- Fabrication costs are less for thick wall vessels. The steel base metal and exterior components can be fabricated using traditional lower cost techniques.
- Components outside of the corrosion envelope, such as half pipes and external jackets, supports, reinforcing pads, stiffeners, and agitator mounts, can be fabricated from low-cost steel.
- Explosion clad zirconium is tough and highly resistant to damage during fabrication or operation. Unlike some non-metallic linings, zirconium clad steel can endure harsh cyclic process operation and upsets, and it is much more resistant to mechanical damage.
- Zirconium can be clad onto whatever base metal is most suitable for the application and process. Although most equipment is constructed of zirconium clad to carbon steel, the base metal can be any common engineering metal. Zirconium can be clad to virtually any grade of stainless steel, copper alloys, nickel alloys, and titanium.
- Zirconium clad can be manufactured in virtually any thickness. Although 3mm to 10mm thickness zirconium cladding is most common, there is virtually no limit to cladding thicknesses that can be supplied. The same applies to base metal, which typically ranges from 12mm to 100mm, but can be much heavier if needed.

Zirconium Clad Process Equipment Applications

Over the past 20 years there has been significant use of zirconium explosion clad components in process equipment. The clad materials have been used primarily as tubesheets in heat exchangers and shell plates and heads for pressure vessels and columns. Equipment fabricated using explosion clad zirconium components has been used extensively in chemical and petrochemical plants. In recent years, several industries have successfully scaled up equipment capacities and capabilities by taking advantage of the features of explosion clad steel.

Applications of zirconium clad manufactured from 1980 to 1997 are reviewed. This summary is an update of information presented in late 1994 (Ref 4) and re-presents much of the earlier information. The analysis was primarily limited to clad manufactured in the United States. This summary is not comprehensive but provides an indication of the level of activity and equipment performance. During this period, clad metal was supplied for over 200 shell and tube heat exchangers, 15 pressure vessels and columns, and one rotary kiln. (The operating details and corrosion conditions presented are accurate to the best of the authors' knowledge. Since much of this information is proprietary, access to this information is limited. If there is any incorrect information presented here, the authors requests to be advised, so that corrections can be made prior to any future updates.)

Application 1

Owner: Domestic Chemical Company
Equipment: Reboiler for methlymethacrylate process
Clad Application: Tubesheets in shell and tube heat exchangers

Corrosive Environment: Sulfuric acid, concentrations varying between 35 and 60% plus unspecified residual components at approximately 150°C
Size: Typical exchanger size is 1.2 to 1.5m diameter by 5m long, TEMA[1] Type BEM design. Tube sheets are typically 1.2 to 1.5m OD by 60mm thick consisting of 10mm thick zirconium 702 clad to 50mm thick carbon steel, ASME SA516 Grade 55.
Unique Features: In this specific acid service, zirconium welds may be susceptible to intergranular attack. This problem is controlled by heat treatment of the welds. The tube-to-tubesheet welds of these units are locally heat treated after welding with a 788°C anneal (Ref 5,6). This heat treatment agglomerates corrosion sensitive grain boundary phases formed between zirconium and residual iron.
Quantity: Over 14 exchangers are in service.
Performance: Some of the units have been in service for more than twelve years. The owner reports excellent corrosion performance.

Application 2

Users. International Chemical Companies in Licensed Nitric Acid Processes
Equipment: Nitric acid cooler condensers
Clad Application: Tubesheets in shell and tube heat exchangers
Corrosive Environment: Nitric acid, 50 to 65% at approximately 11 MPa (160 psi), entering at 230° to 200°C and exiting at 140°C
Size: Exchanger sizes range from 0.4 to 2.0m shell diameter, dependent upon facility needs. Construction is TEMA Type BEM Design. Tubesheets are typically 10mm thick zirconium 702 clad onto steel or stainless steel, thickness ranging from 25 to 100 mm depending upon size. The base steel selection is either carbon steel, ASME SA-516 Grade 70, or stainless steel, ASME SA-240 Type 316L or 304L, depending upon cooling water quality. Figure 2 shows a typical unit during fabrication.
Construction: Most commonly, tubes are rolled into double grooves in the tubesheet and welded to the zirconium face.
Quantity: Over 100 units are in service.
Performance: Excellent corrosion performance is reported.

Application 3

Owners: International Chemical Companies, Licensed Acetic Acid Process
Equipment: Primary reactor for acetic acid manufacture by methanol carbonylation process, mechanically agitated.
Clad Application: Pressure vessel shell plates and heads
Corrosive Environment: Acetic acid and mixed components at 185+°C and "significant positive" pressure
Reactor Size: 3 to 4m diameter by 2.5 to 5m long. Vessel wall thickness consists of zirconium 702, 2.5 to 4.0mm thick, clad onto carbon steel, ASME SA-516 Grade 55, up to 75mm thick.
Quantity: At least three units are in service.
Performance: There are no reports of corrosion problems. The superior corrosion resistance of zirconium has permitted these vessels to operate at "significantly greater efficiencies than the nickel alloy vessels that they have replaced". There have been reports of mechanical damage to the clad surface of one unit resulting from

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[1] Tubular Exchanger Manufacturers Association

agitator blade failure. This has caused consideration of thicker cladding or additional wear plates in selected areas of the vessels.

Application 4

User: International Chemical Company
Equipment: Column for saponification of an organic medium in manufacture of amino acid *Clad Application:* Vessel shell plates and heads
Corrosion Environment: Undisclosed organic acids at temperatures up to 220°C and pressures up to 10 MPa (150 psi)
Vessel Sizes: 2 to 3m diameter by 20 to 25m length. Wall thickness consisting of 3mm thick zirconium 702 clad to 10 to 20mm thick carbon steel, SA-516 Grade 70 or WSTE 355.
Quantity: Several units are in service.
Performance: Excellent corrosion performance is reported. The owner previously experienced problems with stainless steels, titanium, and glass in this environment.

Application 5

User: International Petrochemical Company
Equipment: Column for polypropylene absorption in sulfuric acid
Clad Application: Vessel shell plates and heads
Corrosion Environment: Sulfuric acid solution at 65% concentration with various residual levels of organics and metal ions at approximately 100°C and positive pressure
Vessel Size: 2.3m OD by 12m long; wall thickness consisting of 4 to 5mm thick zirconium 702 clad onto 37mm thick carbon steel, ASME SA516 Grade 55.
Quantity: At least one unit is in service.
Unique conditions: Under these specific environmental conditions, zirconium is potentially susceptible to stress corrosion cracking (Ref 7,8). After completion of fabrication, the complete vessel was stress relieved in the 415° to 440°C range, followed by shot peening of all wetted surfaces.

Application 6

User: International Chemical Company
Equipment: Jacketed reactor with internal agitation, subject to very aggressive thermal and mechanical shock.
Clad Application: Pressure vessel shell plates and heads
Corrosion Environment: Hydrochloric acid, up to 20%, with metal ions present. Operating temperature approximately 110°C.
Unique Fabrication Considerations: To avoid potential stress corrosion cracking problems resulting from ferric chloride presence, the vessel was fully heat treated after fabrication for an extended time at 425°C. Prior to this final heat treatment, the zirconium surface was cleaned with a nitric/ hydrofluoric acid wash.
Reactor Size: 20,000 liters (5,000 gallons)
Quantity: More than one unit is in operation

Performance: Service experience at present is limited; initial inspections indicate that the vessels meet performance expectations. They are expected to perform significantly better in the aggressive mechanical shock environment than the glass lined units that they replace. Figure 3 shows one of these reactors.

Application 7

User: Primary metals manufacturer
Clad Application: Shell plate
Equipment: Rotary kiln for manufacture of zirconium oxide from zirconyl sulfate.
Corrosion Environment: The interior surface of the kiln is ceramic brick lined. The zirconium surface beneath the brick is exposed to surfuric acid and sulfates at temperatures up to 200°C (Ref 9).
Quantity: One unit
Performance: No reports of clad disbonding in cyclic service during 17 years of use.

Additional Applications

Although only one new application has been added to this list since 1994, it should not be assumed that no other new applications have occurred. Zirconium clad has been used in several other new heat exchanger and pressure vessel applications which are not included in this overview.

ZIRCONIUM CLAD FABRICATION

Fabrication and Welding

Zirconium and steel cannot be directly fusion welded to each other due to brittle intermetallic formation. Therefore, clad fabrication is typically accomplished using a batten strap technique as depicted in Figure 4. The zirconium cladding is removed from the area around all edges where steel welds are to be made, usually 12 mm inward from the steel weld prep edge. The steel base metal is prepared and welded using conventional fabrication procedures. Care must be taken to assure that the zirconium surface is not contaminated with steel weld spatter or other detrimental actions. If stress relief of the steel weld is required for Code compliance, it is performed prior to zirconium welding. Nondestructive testing of the steel weld is recommended at this stage. After completion of these operations, a filler-metal strip is inserted into the space from where the zirconium has been removed. The choice of filler is dependent upon proprietary fabrication preferences. Commonly used materials include copper, steel, and zirconium. A wider strip of zirconium, the batten strap, is then placed over the weld area and welded along the edges with fillet welds. Backside purging with inert gas is necessary for reliable zirconium welds. Large diameter nozzles are frequently fabricated from clad plate using these same procedures. Small diameter nozzles are typically loose lined with solid zirconium sleeves. The nozzles and the vessel body are attached using procedures similar to the vessel structure welds with larger batten patches.

Forming of Cylinders and Heads

Clad for vessel shell sections is typically cold rolled or cold formed to the required configuration. Heads are normally formed from clad plate by hot pressing in the 600 to 800°C range, depending upon configuration. Hemispherical heads exceeding about 2m diameter and elliptical heads exceeding 3.1m diameter have been manufactured using segmental construction. Smaller hemispherical heads and elliptical heads have been made by hot pressing a single piece clad blank. Recent new availability of forming tooling makes hot pressing of larger single piece heads possible.

Heat Treatment

For some applications, the corrosion performance of zirconium may be affected by the specific final heat treat condition and by surface contamination during in-process heat treatments. In several of the applications reviewed, a post fabrication heat treatment was performed to achieve specific corrosion performance. In Application 6, and probably others, a specific surface cleaning procedure was used prior to final heat treatment. It is important that the fabricator and the user mutually address these issues prior to equipment manufacture.

CLAD MANUFACTURE

Explosion Cladding

Explosion cladding is the only established process for manufacture of integrally bonded zirconium clad in sizes required for equipment discussed above. The explosion cladding process was commercially developed in the early 1960's. Explosion bonded zirconium-steel clad has been used in process equipment since the late 1960's. Explosion cladding is a solid state metal joining process that uses explosive energy to create a metallurgical bond between the zirconium and steel (Ref 10, 11, 12). Because of the unique safety and noise issues, explosion cladding is performed in relatively isolated facilities by companies specializing in explosives operations. Zirconium clad is supplied to equipment fabricators in the form of flat plates, formed heads, tubesheet blanks, and lined pipe and bar. With the explosion cladding process, zirconium can be clad to virtually any standard engineering metal alloy (in some cases interlayers may be used as discussed below.)

The bond, or weld, created between the zirconium and base metal is similar in strength to the weaker parent metal. In the as-bonded condition, the bond typically does not exhibit sufficient residual ductility for reliable fabrication. A stress relief heat treatment after bonding and prior to fabrication significantly improves ductility. Most clad manufacturers give zirconium clad steel a heat treatment in the 540 to 600°C range.

Cladding Variables and Use of Interlayers

Two variables which significantly affect explosion bonding conditions and resultant bond quality are component metal yield strength and zirconium cladding metal thickness. The effects of these variables are briefly discussed here. References 11 and 12 provide significantly greater detail regarding the relationships between metal properties and explosion bonding parameters.

Optimum bond strength and toughness of zirconium-steel clad is achieved using zirconium with yield strength not exceeding 275 MPa (40 ksi) to carbon steel with a moderate yield strength, such as ASME SA516 Grades 55 to 70. To assure the required yield strength and good ductility, it is common practice to use zirconium with low levels of oxygen (and other strengthening elements). Explosion cladding companies generally prefer to limit oxygen levels in the zirconium cladding plate to 1000ppm.

When higher strength zirconium is needed, or is the only grade available, a thin titanium interlayer is commonly used between the zirconium and steel. Due to the matching crystallographic structures and to the absence of formation of brittle intermetallic compounds, the bond between unalloyed titanium and zirconium is both strong and ductile over a much broader range of component metal strengths. Although titanium is the most common choice, other interlayer metals may be used.

As the thickness of the zirconium cladding sheet increases, the dynamic energy window in which reliable bonding to steel is attainable becomes narrower. Consequently, the control of bonding parameters becomes more critical as the zirconium becomes thicker. The bonding parameter window for welding zirconium and titanium is considerably broader. Consequently, when bonding thicker zirconium to steel, clad manufacturers may chose to use an interlayer. For most clad manufacturers, an interlayer is rarely used with low Ox zirconium at thickness below the 9 to 10mm range, and is commonly used for greater thicknesses. Again, titanium is the most common interlayer choice.

Increasing yield strength of the base steel has a similar effect on bonding parameters. When a steel of greater yield strength than ASME SA516 Grade 70 is needed, an interlayer is generally used. Although stainless steel has a relatively low yield strength, it has a higher work hardening rate than carbon steel, resulting is a significantly greater yield strength increase during bond wave formation. Consequently, the zirconium thickness above which a manufacturer chooses to use an interlayer metal is generally less when cladding to stainless steel as compared to carbon steel.

When interlayers are used, the product can be made by either producing both bonds during a single simultaneous cladding operation or by using a two sequential bonding shots. The single bonding step approach is typically lower cost. At Noblelclad, most zirconium-titanium-steel products are manufactured using a single cladding shot with the titanium interlayer in the 2 to 3mm thickness range.

SPECIFICATIONS AND TESTING

At present there are no ASTM or ASME standards specifically applicable to zirconium steel clad. Explosion clad components are usually produced to proprietary manufacturers' specifications, such as Nobelclad Specification NC501 and IEMA Guidenote 100. Bond integrity is verified using straight-beam ultrasonic inspection procedures, such as ASTM A578. Specifications typically provide several acceptance criteria depending upon the customer's needs, the more stringent being 25 mm maximum length of any indication and 99% minimum sound bond area. Bond strength is normally measured using the shear strength test defined in ASTM A263. The typical specification minimum is 138MPa (20 ksi).

SUMMARY

The review of zirconium-steel clad applications and performance history over the past 17 years indicates reliable equipment performance in environments where zirconium is commonly used. Reliable methods have been established for zirconium clad manufacture and equipment fabrication.

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Figure 1: Cost savings of Zirconium 702 clad carbon steel SA516 Grade 70, compared to solid Zr 702 of equivalent thickness to base steel thickness.

Figure 2: Zirconium-steel clad tubesheet during inspection of tube-to-tubesheet welds. Photograph provided by Phoenix Corp.

Figure 3: External view of zirconium-steel clad pressure vessel, Application 6. Photograph provided by AstroCosmos Metallurgical Corp.

Figure 4: Schematic of batten strap design for joining clad plates during fabrication of zirconium clad equipment.

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