Titanium/Steel Explosion Bonded Clad for Autoclaves and Vessels

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Abstract

Titanium is the material of choice for many highly corrosive chemical process applications. Titanium provides superior corrosion protection in autoclaves and support vessels for pressure acid leaching and pressure oxidation leaching of metal ores. Clad metal construction offers a significant cost reduction for equipment of this type in comparison to solid titanium. Clad metal construction offers superior durability and reliability in comparison with non-metal or titanium loose-lined equipment. With clad construction titanium alloys can be selectively applied in specific areas of the autoclave to accommodate local environmental conditions. The explosion cladding process and titanium alloy selection considerations are discussed in detail. Recent experiences in titanium clad equipment construction and performance are reviewed. The presentation addresses aspects of design, fabrication, and testing which are necessary to assure reliable equipment.

1. Introduction

Titanium’s superior corrosion resistance is ideal for many process applications (Ref 1). Process industries choose titanium as the material of construction for piping, tanks, pressure vessels, autoclaves, and heat exchangers. When pressures and/or temperatures and size demand very thick plate, the titanium equipment can become considerably more expensive than units constructed from lower cost, lower performance materials. Titanium clad steel offers a reliable, cost effective alternative, providing durable titanium lined equipment which is lower cost than many less reliable alternatives. The explosion cladding process produces a high quality titanium-steel clad product with proven fabrication reliability and performance.

2. Pressure Leaching Autoclaves

Hydrometallurgical refining of metal ore is an industry where titanium clad steel has helped to make large scale facilities economically viable. Pressure acid leaching provides an economically viable method for reducing many metal types.
Specifically, sulfuric acid pressure leaching (HPAL) is considered highly cost effective for refining nickel laterite ores, which are low grade but plentiful and easily mined (Ref 2). Autoclaves for HPAL of nickel laterites operate around 250°C to 265°C (480°F to 510°F) and 5.0 MPa (725 psi), using a 5 to 7% sulfuric acid concentration. Corrosion conditions in these facilities are frequently frustrated by high chloride concentrations in the locally available process water. Today’s nickel leaching autoclaves are typically 4m to 5m diameter (150 to 200 in) , 25m to 35m long (80 to 115 ft) with steel wall thickness around 80mm to 120mm (3 to 5 in). In addition to the autoclaves, several of the other vessels in the acid leach circuit operate under similar corrosion conditions. These include flash tanks, slurry tanks, and preheating equipment.

Due to highly oxidizing conditions and low pH, titanium alloys (Ref 3) and refractory brick are the materials of choice for corrosion resistance. Currently accepted material options for construction for these autoclaves are solid titanium, titanium clad steel, and lead-lined steel with internal acid brick linings. Titanium clad steel construction offers many advantages over the other options.

Figure 1: Cost comparison of explosion bonded titanium-steel clad vs solid Titanium Grade 12 of thickness equivalent to steel. Clad is Titanium Grade 17 bonded to carbon steel, SA516 Grade 70. Cladding thicknesses of 4mm (0.16 in) and 8mm (0.32 in) are shown.

In comparison to solid titanium:

1. Titanium clad steel can be considerably lower cost than solid titanium plate. Figure 1 presents a comparison of the costs of clad vs. titanium Grade 12 plate in the thickness range used in nickel laterite processing equipment. For most titanium equipment requiring over 20mm wall thickness, clad reduces cost. As shown, the savings can become very significant for heavy wall vessels.

2. Fabrication costs for titanium clad steel are lower than for solid titanium in the thicknesses typical for autoclaves.

3. Components outside of the corrosion envelope, such as supports, stiffeners, agitator mounts and external jackets can be fabricated from low cost steel.

4. Since titanium is no longer the strength component, the titanium alloy can be chosen for features other than strength, such as corrosion resistance, erosion/abrasion resistance and/or ignition resistance. The designer is no
longer limited to titanium alloys contained in the Pressure Vessel Code table of allowable working stresses.

5. The titanium cladding alloy selection can be varied selectively within the autoclave to provide unique performance features in specific regions of the autoclave.

   > Low cost unalloyed titanium, Grade 1, can be used in regions where general corrosion is the primary concern.
   > Alloys containing palladium or ruthenium, such as Grades 11 or 17, can be used where there is potential crevice corrosion.
   > Highly abrasion resistant alloys, such as Grades 5 or 12, can be used where severe abrasion and erosion are anticipated.
   > Highly ignition resistant alloys, such as Ti-45Nb, can be applied in regions where oxygen impingement or rubbing surfaces pose a potential ignition threat.

In comparison to lead - brick designs:

1. Titanium provides excellent corrosion and abrasion resistance in direct contact with process media at the required operating temperatures and pressures, whereas lead does not. In order to maintain wall temperatures suitably low for lead membrane containment, internal brick linings are 300 to 500mm thick (12 to 20 in.) Titanium eliminates the need for thick refractory brick linings, significantly reducing pressure vessel diameter and weight, shell thickness, welding and fabrication costs, and transportation costs. Current estimates indicate that the cost benefits of size and weight reduction alone more than compensate for the higher materials cost of the titanium clad.

2. Maintenance costs are potentially much lower for titanium clad autoclaves.

3. Titanium Clad Vessels and Performance Experience

Hydrometallurgy Applications: A significant number of titanium and titanium clad pressure vessels have been fabricated for research and production autoclaving over the past 25 years. The largest of these clad autoclaves has been around 3.3m diameter x 13m long (130 x 512 in) (Ref 4). Additionally, many large production autoclaves have employed titanium and titanium clad components in selected areas. However, until recently, no large production autoclaves have been constructed of titanium or titanium clad. During 1996 and 1997 six large titanium clad nickel laterite autoclaves were fabricated. These vessels were 4.8 to 5.0m (189 to 197 in) diameter x 30m to 35m (98 to 115 ft) long. One of the six is clad with Titanium Grade 11 (Centaur-Cawse); one with Grade 17 (Resolute-Bulong); and four with Grade 1 (Anaconda-Murin Murin); base steel is ASTM A516 Grade 70. Cladding thicknesses range from 6mm to 8mm (0.24 to 0.32 in), and base thickness is typically 100mm (4 in). Figures 2 shows one of these autoclaves at the completion of fabrication. These vessels are all expected to be in service or in commissioning at the time of this presentation. Projected autoclave service life is 20 years minimum.

General Chemical Process Applications: Pressure vessels of similar size and construction to the autoclaves have been used in the chemical process industries for many years. Since the late 1960’s titanium explosion clad has been the standard material of construction in the chemical process industry when titanium corrosion resistance is required in combination with high pressures and/or high temperatures. Chemical and petrochemical process companies have installed hundreds of pressure vessels and thousands of heat exchangers fabricated from titanium explosion clad. A large portion of these units has been installed in petrochemical plants producing terephthalic acid (TA) and purified terephthalic acid.
(PTA.) TA and PTA are building block chemicals for the manufacture of polyester. In the past two decades these plants have proliferated around the world. These require agitated reactors which operate at temperatures between 200°C (390°F) and 250°C (480°F) and maximum pressures of 2.34MPa (340psi). Traditionally these vessels have had excellent low maintenance performance records. The trend has been to increasingly larger vessels and higher temperatures, resulting in a significant advantage using clad construction. Several titanium clad PTA reactors of over 7.7m (300in) diameter and 75mm (3in) wall thickness have been placed in service in recent years. Two major differences between the PTA vessels and the laterite autoclaves are titanium cladding thickness and orientation. The PTA reactors typically use a 2 to 3mm thick titanium cladding layer. The recent group of laterite autoclaves use a 6mm to 8mm titanium cladding thickness in anticipation of potential erosion conditions. The PTA reactors are vertical, requiring more difficult transport and erection.

Figure 2: Titanium clad autoclave for nickel laterite pressure acid leaching. The autoclave is Titanium Grade 1 clad steel for the Murin Murin Nickel / Cobalt Project. Photo provided by the autoclave fabricator, ASC Engineering, Adelaide, Australia.

4. Explosion Clad

Process Overview: Explosion cladding is a solid state metal-joining process that uses explosive force to create an electron-sharing metallurgical bond between two metal components. Although the explosive detonation generates considerable heat, there is no time for heat transfer to the component metals; therefore, there is no appreciable temperature increase in the metals. Due to the absence of heating, the microstructures, mechanical properties and corrosion properties of the wrought parent components are not significantly altered during explosion bonding. There are no heat affected zones, and brittle intermetallic layers are not formed. For these reasons explosion cladding is ideally suited for bonding of virtually any combination of metal. (Ref 5,6,7). Titanium and iron are not metallurgically compatible at high temperatures. Under conditions normally used for weld overlay or hot rollbonding, titanium and steel instantly react to
form brittle intermetallic compounds. Consequently, explosion cladding is the preferred process for manufacture of titanium clad steel.

Figure 3 presents a schematic of the explosion bonding process. During the bonding operation the titanium plate is accelerated toward the steel plate by the explosive detonation energy. The plates collide under high velocity oblique conditions generating a jet of metal being stripped from the colliding metal faces. Surface contaminants which normally prevent pressure bonding are removed in this jet. The result is a high strength metallurgical bond. Figure 4 shows a typical explosion bond interface. The dynamic bonding conditions result in a wavy bondzone morphology; a characteristic footprint of a high quality explosion bond.

Figure 3: Schematic depiction of the explosion cladding process. (a) Explosion cladding assembly before detonation. (b) Explosion cladding assembly during detonation. (c) Close-up showing removal of surface contaminants in jet. (Ref 6)

Because of the unique safety and noise/vibration considerations, explosion cladding is performed in relatively isolated facilities by companies specializing in explosive clad manufacture. At the time of this presentation, there are three clad manufacturing companies worldwide with proven experience in the product sizes required for cost effective HPAL autoclave construction. Manufacturing processes for all are similar but specific process parameters are proprietary. Product sizes are normally limited only by the size availability of the component metals and the explosive detonation limitations of the manufacturing facility. For most cladding metals types (including titanium), cladder sheets can be butt welded together prior to cladding, permitting production of clad plates much larger than available cladding metal sheet sizes. Explosion clad materials are typically supplied to equipment manufacturers in the form of flat plates and discs, formed heads, and cylindrical shapes.

During the explosion cladding operation, the bondzone wave formation results is significant localized cold work, creating a bond which exhibits high strength but low ductility. It is standard practice to stress relieve titanium/steel clad in the 538°-635°C (1000°-1175°F) range to optimize bond toughness prior to proceeding with fabrication.
Titanium clad plates with widths of 4.5m (176in) and lengths of 11m (430in) are commonly produced. The titanium cladding thickness typically ranges between 2mm (0.08in) and 19mm (0.75in), dependent upon the application. The steel base metal typically ranges between 12mm (0.5in) and 500mm (20in), dependent upon pressures.

Titanium/Steel Clad Specifications and Testing: Since the titanium is not part of the design strength allowance, ASME Code (or AS1210) compliance is only required for the base steel. There are currently no ASTM or ASME standard specifications specifically for titanium clad. Titanium clad is normally produced to manufacturer's or purchaser's proprietary specifications, for example Nobelclad Specification NC501. (At the time of this presentation, an ASTM Task Force has been established to develop a titanium clad specification with anticipated completion in 1999.)

Shear strength testing is the most common method for determining bondzone mechanical properties. The test design and method presented in ASTM A-264 are standard. Most specifications require a minimum value of 137mpa (20,000 psi). Bond shear strengths for titanium-steel are typically in the 240 MPa (35,000 psi) to 340MPa (50,000 psi) range with average values of 270 MPa (39,300).

The bond integrity of clad metals is normally inspected using ultrasonic testing (ASTM A578). For autoclaves, specifications normally require inspection of 100% of the clad surface and a minimum sound bond area of 99% (ASTM A578 S7).
Titanium and Steel Alloy Options: All of the titanium alloys can be clad using the explosion bonding process. However, the optimum bond mechanical properties and optimum plate sizes are produced when the yield strengths of both the cladding and base metal are below 345 MPa (50,000 psi). Consequently the optimum bond strength and toughness of titanium cladding results from a combination of Titanium Grade 1, or similar, clad to a moderate strength pressure vessel steel, such as ASME SA516 Grade 70. (Titanium Grades 17, 11, and 27 exhibit similar yield strength and similar bond performance to Grade 1.) Although higher strength titanium alloys such as Grades 2 and 12, can be directly bonded to steel, the maximum sizes that can be manufactured reliably are too small for cost effective manufacture of HPAL autoclaves. When cladding higher strength titanium grades in large plate sizes, it is common practice to use an interlayer metal between the alloy titanium and steel. Grade 1 titanium is the most commonly used interlayer for clad pressure vessel applications. Alternately, other alloys can be applied to the Grade 1 base using processes such as weld overlay or strip cladding. For example, in regions of a vessel requiring high erosion resistance, Grade 5 or 12 can be weld overlay deposited onto Grade 1 cladding, or wear plates can be welded directly to the Grade 1 cladding. Table I lists several of the currently available titanium alloys and highlights their specific features including cladability and relative cost of the clad product (Ref 4,7).

<table>
<thead>
<tr>
<th>Gr#</th>
<th>Basic Alloy Components</th>
<th>Cladability</th>
<th>Cost (**)</th>
<th>Features/Motivation for Alloy (****)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti (Chem. Pure)</td>
<td>Direct</td>
<td>1.0</td>
<td>Low Cost, High ductility</td>
</tr>
<tr>
<td>2</td>
<td>Ti (less pure)</td>
<td>Interlayer</td>
<td>1.5</td>
<td>Low Cost, Medium Strength</td>
</tr>
<tr>
<td>3</td>
<td>Ti (less pure)</td>
<td>Interlayer</td>
<td>1.6</td>
<td>Low Cost, Higher Strength</td>
</tr>
<tr>
<td>5</td>
<td>Ti+6AL+4V</td>
<td>Interlayer</td>
<td>1.7</td>
<td>Strong &amp; Erosion Resistant</td>
</tr>
<tr>
<td>7</td>
<td>Ti Gr2+0.15Pd</td>
<td>Interlayer</td>
<td>1.9</td>
<td>Crevice Corrosion Resistance</td>
</tr>
<tr>
<td>11</td>
<td>Ti Gr1+ 0.15Pd</td>
<td>Direct</td>
<td>1.4</td>
<td>Crevice Corrosion Resistance</td>
</tr>
<tr>
<td>12</td>
<td>Ti+.3Mo+.8Ni</td>
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<td>Strong and Erosion Resistant</td>
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<tr>
<td>16</td>
<td>Ti Gr2 + .05Pd</td>
<td>Interlayer</td>
<td>1.7</td>
<td>Crevice Corr. Resist. Lower $</td>
</tr>
<tr>
<td>17</td>
<td>Ti Gr1 + .05Pd</td>
<td>Direct</td>
<td>1.2</td>
<td>Crevice Corr. Resist. Lower $</td>
</tr>
<tr>
<td>27</td>
<td>Ti Gr1 + .1Ru</td>
<td>Direct</td>
<td>1.1</td>
<td>Crevice Corr. Resist. Lower $</td>
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<tr>
<td>NA</td>
<td>Ti-45Nb</td>
<td>Direct</td>
<td>2.3</td>
<td>Excellent Ignition Resistance</td>
</tr>
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</table>

Legend:
* ASTM B265 Grade Designation
** Readily explosion clad direct to steel, or interlayer recommended
*** Clad Metal Cost Ratio in comparison to Lowest Cost Alloy (Ti Gr 1/steel), Based upon 8mm thick titanium alloy clad onto 100mm thick steel.
**** When Alloy Composition shows “Ti Gr.# + addition”, the alloy exhibits features of the base Grade plus the features listed for the higher grade.

5. Titanium Clad Equipment Manufacture

Titanium clad equipment can be reliably constructed and has proven service reliability. However, due to differences in metallurgical characteristics, thermal expansion, modulus, and other aspects, titanium clad construction is not just
another clad vessel.” Special considerations must be taken in design, fabrication, welding, and testing to insure a reliable product. Inadequate attention to proper design and fabrication techniques can result in a subsequent vessel failure.

Weld Joint Design: Titanium and steel cannot be directly fusion welded to each other due to brittle intermetallic formation. Clad fabrication is typically accomplished using a batten strap technique as depicted in Figure 5. The titanium cladding is removed from the area around all edges where steel welds are to be made, typically 12mm (0.5in) inward from the steel weld prep edge. The steel base metal is prepared and welded using conventional steel fabrication procedures. The vessel is then cleaned up and prepared for titanium welding. In the batten strap technique, a filler-metal strip is inserted into the space where the titanium has been removed. The choice of filler is dependent upon proprietary fabrication preferences; commonly used materials include copper, steel, aluminum and titanium. A wider strip of titanium, the batten strap, is then placed over the weld area. The batten strap is welded along the edges with fillet welds. Large diameter nozzles are frequently fabricated from clad plate using these same procedures as for vessel fabrication. Typically, smaller diameter nozzles are lined with solid titanium or bimetallic titanium-steel sleeves. Attachments between nozzles and the vessel body are made using procedures similar to those employed on the vessel circumferential and longitudinal butt welds.

Figure 5: Schematic of titanium clad fabrication using Batten Strap method.

Although the above description is quite simple, the precise design of welds and batten straps for autoclaves is not. One critical concern results from the highly different thermal expansions of titanium and steel combined with the high operating temperatures of the equipment. The coefficient of thermal expansion (CTE) of titanium is 30% lower than that of carbon steel. Since the thickness of titanium is typically only 5% to 10% of the steel thickness, the titanium is essentially forced to move at the steel CTE rate. This strain results in a tensile stress in the titanium cladding layer. Over the main body of the autoclave, the continuous clad bond transfers the thermal expansion stresses between the two metals uniformly. In the weld region, all of the differential stress must be borne by the batten strap and the fillet welds along each edge. Incorrect design can result in stresses in the welds that exceed proper design allowables, and that could potentially result in catastrophic weld failure in service. Experience has
shown that properly designed weld systems are problem free in service. It is
critical that detailed stress analyses and experimental verification be performed
to assure proper sizing and configuration of the batten straps and the fillet welds
joining them to the clad plate surface. Specific details are typically highly
protected proprietary designs of the equipment fabricators. It is not the purpose
of this paper to provide a detailed discussion of vessel stress analysis and the
authors have minimal expertise in this area; however, for successful vessel
performance the importance of this aspect of vessel design cannot be over
emphasized.

Forming: During vessel fabrication the clad plates are formed into cylinders and
heads. Cylinder rolling is either performed near ambient temperature or in the
temperature range of 540°C to 650°C (1000°F to 1200°F), dependent upon
forming equipment capability. Hot pressing is the preferred head forming
technique. Forming in the 540°C to 650°C (1000°F to 1200°F) range is
preferred. At these temperatures intermetallic formation is sluggish; the operator
can concentrate on producing a good head, not on getting it done quickly. If
needed, higher temperatures can be used, but forming temperatures must be
maintained below 815°C (1500°F) and hold times at this temperature must be
minimized to about 2 hours to avoid gross intermetallic formation and bond
failure.

Fabrication and Welding: The fabrication of titanium clad vessels requires
special precautions. The steel portion of the fabrication process is typically
dirty, producing large amounts of metal dust, swarf and sparks. The titanium
portion of the fabrication process must be clean. During steel fabrication
titanium surfaces must be protected from grinding, welding and cutting sparks to
avoid localized iron contamination of the clad surface. After this aspect of
fabrication, and before stress relief heat treatment, all iron surface contamination
must be removed by grinding or similar processing. Surface cleanliness can be
verified by ferroxyl testing. Unless proper cleaning is performed, residual iron
surface contamination can alloy with the titanium during the stress relief heat
treatment, causing localized loss of corrosion resistance.

After steel fabrication and heat treatment, and prior to titanium welding, it is best
to transfer the vessel to a clean shop. Alternatively, since vessels are normally
clad on the inside, the interior of a clean clad steel vessel can provide suitable
conditions for titanium welding, once the openings are sealed off. Care must be
taken to assure that contamination from the steel welding shop is not dragged in
later. Additionally safety precautions must be taken to prevent accumulation of
deadly levels of inert gas in the work area.

Titanium welding is not difficult, but the concerns are very different than with steel
welding. (Ref 9) At high temperatures, titanium will react with virtually everything
except the inert gases. Above 425°C (800°F), titanium will readily absorb oxygen;
the absorbed oxygen makes the titanium brittle and mechanically useless. Even
very small amounts of oxygen (0.8%) will totally embrittle titanium. At welding
temperatures, titanium will react with water, disassociate the water molecules, and
then absorb the oxygen atoms. Cleanliness, freedom from moisture, and
protection with an inert gas cover are absolutely critical for successful titanium
welding. Since titanium will react with oxygen well below the melting point, it is
important to maintain inert gas shielding of the weld area until it has cooled below
at least 300°C (575°F). For the batten strap welds, backside purging with inert gas
is also mandatory to prevent oxygen contamination of the weld from the root side. Note the backside purge hole in Figure 5.

Titanium welds that have been contaminated by oxygen exhibit two readily discernable features. They exhibit obvious discoloration and increased hardness. Good titanium welds are shiny silver to slightly straw color. Contaminated welds are blue to grey to white in the worst case. Welders must learn to read the color of their welds, and to immediately reject areas where weld color indicates a defective weld. Areas of contaminated weld cannot be repaired by welding over the defective area; the contaminated area must be fully removed before a successful replacement weld can be made.

With proper training, equipment, and attention to detail, reliable high-quality titanium welds can be assured.

6. Inspection and testing

The steel welds are inspected by traditional steel fabrication inspection methods. Inspection of the titanium batten strap welds requires different methods. One of the concerns with the batten strap fillet weld design is that it cannot be reliably inspected by radiography, the traditional weld inspection process. One major concern is weld root quality; test methods may vary between vessel fabricators. Surface defects can be detected by penetrant testing. Gross weld defects can be isolated by pressure testing with helium. The high pressure gas can be fed behind the weld through the inert gas purge holes; leakage can be monitored on the opposite weld surface. Hardness measurements should be taken at periodic locations to test for contaminated titanium welds.

Ambient temperature hydrostatic testing is necessary for code compliance, but it will do little to reveal defects or problems with the titanium welds and batten straps. This is a particular concern when the vessel will be operating at high temperatures, as are the autoclaves. Hot, high pressure cycle testing, simulating the operating temperatures and pressures is highly recommended for locating isolated weld defects or batten strap problems. Considering the very large amount of welding in an autoclave, some weld rework is to be anticipated. The equipment should be given a series of cycles simulating temperature and pressure service conditions with intermediate penetrant and helium leak inspections. Weld defects should be reworked, and the complete process repeated. For a number of reasons, it is preferable to perform this testing in the fabricator’s shop prior to shipment of the vessel. However, with the very large autoclaves this may not be practical; the cost of equipment and facilities for shop testing can be huge. It may be preferable to perform these tests after delivery to the site since the process steam facilities are available there to provide both heat and pressure. This can be done effectively if the fabricator and the procurement engineers work together to plan this in the pre-commissioning schedule. Testing of this type will assure correction of design, fabrication, and/or welding defects, minimizing problems in startup and subsequent operation.

7. Conclusion

Titanium clad solves corrosion, maintenance and environmental problems in many reactor and autoclave applications. Titanium clad construction permits autoclave designers a great deal of flexibility combined with significant cost reduction. Titanium alloys can be selectively applied in specific regions of the
auto clave to maximize performance under anticipated localized environmental conditions at minimal cost. Explosion clad pressure vessel fabrication and performance have been demonstrated through three decades of experience. With proper attention to design, fabrication methods and testing, titanium clad equipment is highly reliable, durable, and long lasting.

References


