

**Presented at Reactive Metals in Corrosive applications Conference
Sun River, OR, USA September 12-16, 1999**

Hydrometallurgical Applications of Titanium Clad Steel

J.G.BANKER
CLAD Metal Products, Inc.
PO Box 11313
Boulder, Colorado 10301 USA
Phone 1-303-581-0621
FAX 1-303-581-9481

Abstract

Titanium is the material of choice for corrosion control in many hydrometallurgy processes. 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. Experiences in titanium clad equipment construction and performance are reviewed.

Introduction

Historically, pyrometallurgical processes have been the dominant methods for recovering metals from their ores. Typically ores have been roasted and smelted to extract their metal content. These processes have tended to be major air polluters. Compliance with anti-pollution regulations of recent decades has necessitated extensive costly equipment additions. Considerable research has been devoted to development of alternate processes to lower the environmental and financial costs of metal reduction.

For many metals hydrometallurgical processes provide a lower cost alternative. These processes typically involve leaching the ores with aqueous solutions of common mineral acids. Acid leach or pressure-acid leach (PAL) processes have become commercially viable for extraction of copper, gold, nickel, uranium, molybdenum, zinc and other metals. (Ref 1)

Hydrometallurgical processes can range from relatively low-tech heap operations to much more sophisticated high pressure processes performed in large autoclaves (big pressure cookers.)

The aggressive acid environments of most leaching processes present significant corrosion issues for their containment materials. Low temperature-pressure processes, such as heap leaching, are commonly contained with plastics or other non-metallics. The high temperatures and pressures of the pressure leaching processes generally require containment in metal pressure vessels, commonly called autoclaves. Corrosion issues necessitate that the autoclaves either be constructed of corrosion resistant alloys or be lined with ceramics or corrosion resistant alloys.

Oxygen is commonly a second major component of the pressure acid leaching processes. The combination of oxygen and multivalent metal ions in the ore solutions provides an environment in

which titanium frequently exhibits excellent corrosion resistance. Consequently titanium has become the metal of choice for many pressure acid leaching processes (Ref 1).

When pressures and/or temperatures and size demand very thick plate, the titanium equipment can become quite expensive. 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.

Titanium In Early Autoclave Applications

Titanium and titanium clad have been used in construction of pressure acid leaching autoclaves since the 1950's. Table 1 presents a list of test autoclaves and smaller production units that were constructed of titanium or titanium clad in the 1970's and 1980's. Reference 1 presents additional information on use of titanium components in primarily refractory lined autoclaves dating back to the mid 1950's. The reliable performance of these units led to later use of titanium and titanium clad in subsequent larger production autoclaves.

Table I

Titanium and Titanium Clad Autoclaves pre 1985 (Ref. 2)

Date Installed	Type	# Units	Design *	Size (OD x L) (m)	Temp (Deg.C)	Press. (Mpa)	Process (Note)
1970	Ti Clad	2	C/H/4	3.3 x 13.2	121	517	1
1970	Ti Clad	2	C/H/4	3.3 x 13.2	200	1900	2
1975	Ti Clad	1	C/H/3	1.8 x 5.4	140	1380	3
1975	Ti Clad	1	C/H/3	1.8 x 5.4	140	1380	3
1976	Ti	3	C/H/7	3.0 x 29.0	140	517	4
1976	Ti Clad	3	B/V/1	2.4 x 4.5	160	1034	3
1982	Ti	2	B/V/1	1.1 x 2.4	-		5
1984	Ti	1	C/H/4	0.75 x 3.6	-		6

* Design: C= Continuous B=Batch #=Number of Compartments
H= Horizontal V=Vertical

Process Notes:

- | | | |
|------------------------|--------------------------|------------------------|
| 1. Acid Zn Leach | 2. Acid Fe Precipitation | 3. Acid Ni-Cu-Co Leach |
| 4. Acid Cl Leach of Cu | 5. Acid Co-Cr-Ni Leach | 6. Acid S/C Cu Leach |

Production Autoclaves for Gold

In the 1980's the first large pressure oxidation leaching operations were constructed for extracting gold from refractory ores. Table 2 lists many of these projects. By the mid 1990's at least 12 production autoclaves had been put in service, the largest being approximately 19-ft ID x 80-ft long (5.8 m x 24 m). These autoclaves operate in the horizontal position with the process liquor cascading

across several agitated chambers as it flows through. The gold autoclaves operate in the 210C and 300 psi (2 Mpa), temperature and pressure range. The process uses sulfuric acid at concentrations around 5% with oxygen injection to high partial pressures. The autoclaves are steel construction with an internal corrosion membrane of lead protected by refractory brick linings in the 8 to 12 in (200-300mm) thickness range. Titanium use has been minimized by concerns over ignition of non-wetted components in the presence of high oxygen levels. Agitator shafts and blades are commonly titanium construction. Some units utilize titanium baffles to separate process chambers. Most use titanium clad steel plates for the agitator mounting flanges. Titanium-45 Niobium has become a material of choice for oxygen injection tubes.(Ref 3) With proper design and operation, titanium has performed well.

Several engineering cost studies have been performed comparing lead and brick pressure oxygen leaching autoclaves with clad steel. These clad units have consisted of titanium clad steel for the wetted components and Titanium-45 Niobium clad steel for the nonwetted components. Projected capital costs for the two options are comparable. Current indications, based upon the nickel autoclave experience presented below, are that maintenance costs for the clad autoclaves will be significantly lower than for brick lined units.

Table II
Gold Pressure Leaching Projects which have used Titanium and /or Titanium Clad Internals, Agitators, or Piping

Cominco	Trail, British Columbia, CANADA
Kidd Creek Mines	Timmins, Ontario, CANADA
Homestake-McLaughlin Mine	California, USA
Sao Bento Mineraco	Belo Horizonte, BRAZIL
First Miss Gold-Getchell Mine	Winnemucca, Nevada, USA
American Barrick-Goldstrike Mine	Elko, Nevada, USA
Placer Dome-Porgera Mine	Papua, NEW GUINEA
Placer Dome-Campbell Mine	Balmerton, Ontario, CANADA
Hudson's Bay Mining & Smelting	Flin Flon, Manitoba, CANADA
NERCO-Con Mine	Yellowknife, N.W.T., CANADA
Santa Fe Mining, Lone Tree	Valmy, Nevada, USA
Santa Fe Mining, Twin Creeks	Winnemucca, Nevada, USA
Niugini Gold	Lihir Island, Papua, NEW GUINEA

Production Autoclaves for Nickel

Technology for pressure acid leaching of nickel from laterite ores was initially developed by Sherritt in the late 1950's at Moa Bay, Cuba.(Ref 4) The Cuban facilities included extensive use of titanium and titanium clad components. In Australia in 1996 construction was begun on the first large production plants for pressure acid leaching of nickel laterites. The autoclaves in these plants are similar in design to those in the gold plants. However, several major differences drove the material of construction decision to titanium clad steel. The process does not use oxygen injection. The operating temperature is higher at 250 to 260C and the pressure is higher at 700 to 750 psi (4.8 to 5.2 MPa). At these lower oxygen concentrations, titanium ignition is not an issue. At the higher temperatures, the

required brick thickness is appreciably greater, significantly increasing capital and maintenance costs. For these vessels titanium clad steel was the low cost material of construction.



Figure 1: 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.

By early 1999 six titanium clad autoclaves were in operation at three nickel laterite refineries in Western Australia. These autoclaves are typically 16 ft dia. x 98 to 115 ft long (4.8 m dia x 25 to 35 m) with 4in (100mm) thick steel, and weighed in the 1,000,000 pound range (450 metric tons). They are the largest, heaviest titanium clad vessels that have been constructed to date. At the time of this presentation, operational performance of the titanium clad autoclaves is considered excellent. (Ref 5) Current designs for future plants and modifications of the existing plants include application of titanium and titanium clad in additional plant equipment, including flash tanks and other heat transfer equipment. Table III presents data on autoclave size, titanium alloy and mine site.

Table III

Australian Nickel Laterite PAL Autoclaves

Project	Owner	Qty	Size (m)	Titanium Selected
Bulong	Preston Resources	1	4.60 ID x 31 long	Gr 17 8 mm thick
Cawse	Centaur Gold	1	4.65 ID x 27 long	Gr 11 8 mm thick
Murin Murin	Anaconda Nickel	4	4.95 ID x 35 long	Gr 1 6 mm thick

Materials Options for Nickel PAL Autoclaves

Due to highly oxidizing conditions and low PH of nickel laterite leaching, titanium alloys and refractory brick are the materials of choice for corrosion performance. 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.

In comparison to solid titanium:

1. Titanium clad steel can be considerably lower cost than solid titanium plate. Figure 2 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.

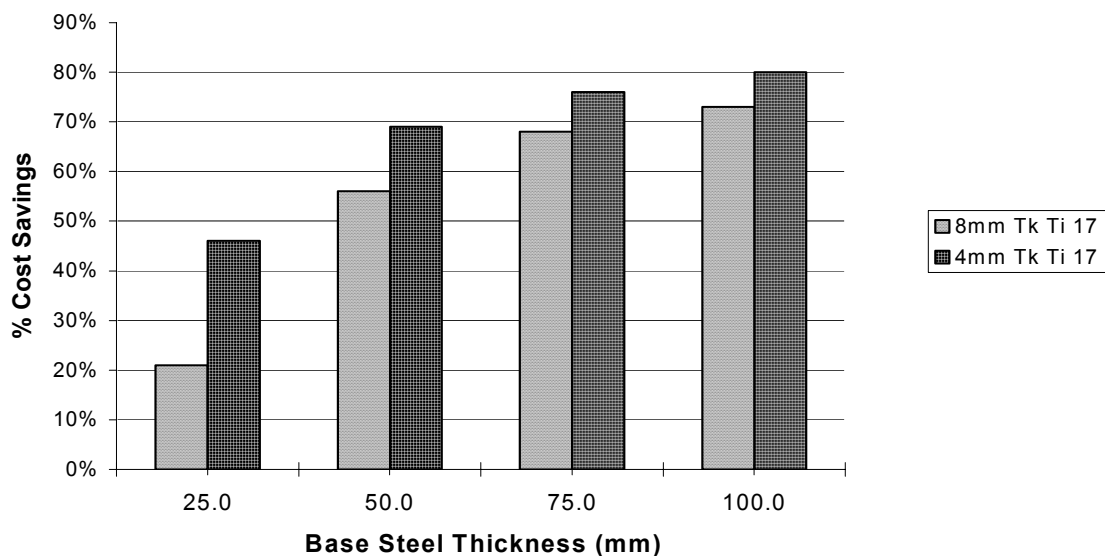


Figure 2: Cost comparison of explosion bonded titanium-steel clad vs solid Titanium Grade 12 of thickness equivalent to steel. Clad is Titanium Grade 17 bonded to carbon steel, SA516 Grade 70. Cladding thicknesses of 4mm (0.16 in) and 8mm (0.32 in) are shown.

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, 17, or 27, 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.

Explosion Clad

Titanium clad steel for the autoclave construction is produced by the explosion cladding process. Explosion cladding is a solid state metal-joining process that uses explosive force to create a 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 of the metals. The process is ideal for joining metals which are not compatible at elevated temperature, such as titanium and steel. 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. (Ref. 6,7,8)

Because of the unique safety and noise/vibration considerations, explosion cladding is performed in relatively isolated facilities by companies specializing in explosive clad manufacture. Product sizes are normally limited only by the size availability of the component metals and the explosive detonation limitations of the manufacturing facility. Explosion clad materials are typically supplied to equipment manufacturers in the form of flat plates and discs, formed heads, and cylindrical shapes.

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 clad is normally produced to ASTM B898 or manufacturer's proprietary specifications.

For additional information on the explosion cladding process, please turn to the referenced literature or visit the Nobelclad internet site, www.Nobelclad.Snpe.com.

Titanium and Steel Alloy Options for Cladding: 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 PAL 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 IV lists several of the currently available titanium alloys and highlights their specific features including cladability and relative cost of the clad product.

Table IV
Selected Titanium Alloys and Performance Features (Ref. 9,10)

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

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.

Titanium Alloy Considerations for Corrosion Performance: As shown in Table III, the different nickel laterite projects have selected different titanium alloys for corrosion control. The water at the Bulong and Cawse sites is very high in chlorides. The palladium containing alloys, Grades 17 and 11 respectively, we selected due to concerns over chloride induced crevice corrosion. The Murin Murin project has a near chloride free water source. Use of the higher cost, longer delivery palladium alloys was considered unnecessary under these conditions. Where the specific corrosion environment is not obvious, the palladium or ruthenium containing alloys (Grades 11, 17, 27) are considered to be a more conservative choice. (Ref 9, 11)

Titanium Clad Equipment Manufacture

Titanium clad equipment can be reliably constructed and has proven service reliability. Well over 1,000 titanium clad pressure vessels have been placed in service over the past 35 years. 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. Information on titanium welding and titanium clad fabrication, testing, and inspection procedures has been relatively broadly published. (Ref's 10, 12)

Conclusion

Titanium clad solves corrosion, maintenance and environmental problems in many hydrometallurgy 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 autoclave 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

- 1) Shutz, R.W., & Covington, L.C., "Hydrometallurgical Applications of Titanium" Industrial Applications of titanium and Zirconium, ASTM STP830, R.T.Webster & C.S.Young. American Society for Testing and Materials, 1984, pp29-47.
- 2) Banker, J.G., Forrest, A.L., "Titanium/Steel Explosion bonded Clad for Autoclaves and Reactors", Proceedings of Randol Gold Forum '96, Randol Corp., Golden, CO, 1996.
- 3) Krag, P.W. and Henson, H.R., "Materials Selection for Sulfide Pressure Oxidation Autoclaves," Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres, ASTM STP 1197", Dwight D. Janoff, and Joel M. Stoltzfus, Eds., American Society for Testing and Materials, Philadelphia, 1993.
- 4) Chalkley, M.E. et al, "The Acid Pressure Leach Process for Nickel Cobalt Laterite: A Review of Operations at Moa Nickel S.A." Presented at Nickel Cobalt Pressure Leaching and Hydrometallurgical Forum, Perth, WA, May 13-14 ,1996.
- 5) O'Shea, John, Nickel Australasia, O'Shea & Associates, Melbourne, Australia, Issue 28, Aug. 1999,
- 6) Pocalyko, A., "Explosively Clad Metals," Encyclopedia of Chemical Technology, Vol. 15, Third Edition, John Wiley & Sons, 1981, pp 275-296.
- 7) Banker, J.G., Reineke, E.G., "Explosion Welding", ASM Handbook, Vol. 6, Welding, Brazing, and Soldering, 1993, pp 303-305.
- 8) Nobili, A., "Explosion Bonding Process", Nobelclad Technical Bulletin, Nobelclad, Paris La Defense, France, March 1999
- 9) Schutz, R.W., "Recent Titanium Alloy and Product Developments for Corrosive Industrial Service," National Association of Corrosion Engineers, Corrosion 95, Paper No. 244.

- 10) Banker, J.G., Winsky, J.P, “Titanium/Steel Explosion Bonded Clad for Autoclaves and Vessels,” Alta 1999 Autoclave Design & Operation Symposium, Alta Metallurgical Services, Melbourne, Australia, May 1999.
- 11) Grauman, J, S. and Say, T., “Understanding the Behavior of and Preventing Problems with Titanium in Hydrometallurgical Pressure Leaching Equipment,” Alta 1999 Autoclave Design & Operation Symposium, Alta Metallurgical Services, Melbourne, Australia, May 1999.
- 12) Titanium Welding Handbook and Video, International Titanium Association, Boulder, CO, 1994.

Key Works

Explosion Clad

Titanium Clad

Pressure Acid Leaching

Nickel Laterites

Autoclaves

Pressure Vessels