ZIRCONIUM CLAD PRESSURE VESSELS OFFER COST SAVINGS IN HIGHLY CORROSIVE HCL SERVICE

David Frey
Astro Cosmos Metallurgical Co.
835 Flynn Road
Camarillo, CA USA
e-mail: david.frey@astrocosmos.com
Phone: 1.805.482.9825
Fax: 1.805.987.7961

John G. Banker, V.P., DMC Clad Metal Div.
5405 Spine Road
Boulder, CO 80301 USA
e-mail : jbanker@dynamicmaterials.com
Phone : 1.303.604.3915
Fax : 1.303.604.1893

Presented at Wah Chang Reactive Metal Conference, 12 September 2001. Proceedings to be published in late 2001.

ABSTRACT

Zirconium clad steel reactors have demonstrated superior performance to glass lined steel reactors in an aggressive process application at a major chemical company. The environment is severe with hot, corrosive hydrochloric acid containing ferric ions, thermal and mechanical cycling, mechanical agitation, and external heat transfer jacketing. The service life of glass lined vessels required reglassing or replacement within fifteen months. Zirconium clad vessels were fabricated for direct replacement of the glass lined units. To date, several of the zirconium clad vessels are in service, some for over four years. Zirconium clad construction is approximately half the cost compared to solid zirconium units and provides positive cost-performance benefits in comparison to glass. The presentation includes discussion of the materials selection process, fabrication and clad manufacture issues as well as details of material performance.

KEY WORDS

Zirconium, Clad, Reactor, HCL

INTRODUCTION

For more than 20 years the Owner's production facilities had been using steam jacketed glass-lined steel reactors in a critical service, with recurrent problems. The glass-lined steel vessels were lasting an average of fifteen months before reglassing or total replacement, and required a sizeable maintenance structure to perform interim repairs and rapid changeouts with a large spares inventory to minimize downtime. Short service life was due to the corrosive nature of the environment, demanding operating conditions, and the typical mechanical damage associated with glass-lined steel equipment. Reliability improvement efforts provided only small gains. Use of an alternative material of construction was seen as the only way to effect a needed step change improvement.

MATERIAL SELECTION

In the mid 1990's the Owners engineers met with material and design engineers from DMC, AstroCosmos, and Wah Chang to explore the potential of using reactive metals in the problem application. This "team" developed an action plan that would show that a reactive metal clad vessel was the optimum material of choice for the service. This unique approach appeared necessary because of the safety and environmental criticality of the application to the Owner. Zirconium was determined to be the best candidate material of construction. However, some earlier testwork indicated some significant obstacles to overcome: during in situ testing of zirconium 702, stress corrosion cracking (SCC) was observed in test coupons. It was believed that ferric chloride was the SCC promoter. Since freedom from ferric chloride contamination could not be assured, a solution to the SCC issue had to be developed.

It was believed that the corrosion could be mitigated by proper vessel design and fabrication, and by proper process controls. In laboratory corrosion tests, zirconium 702 samples were exposed to the simulated process environment with differing ferric chloride concentrations. All tests were conducted for 984 hours at a temperature simulating the process. All coupons were welded and then formed into U-bend SCC test specimens. One group of specimens was tested in the as-stressed condition, the other group was given a stress relief heat treatment prior to exposure. These lab corrosion tests demonstrated that low concentrations of ferric chloride were not likely to initiate SCC under any conditions, and that even higher concentrations of ferric chloride were not likely to initiate SCC if the zirconium was in a stress relieved condition. In addition, the tests indicated that stress relieved zirconium would experience no general or localized corrosion, Table I

Table I: Corrosion vs. Process and Stress Relief Variables

A. Reaction mass with low ferric chloride concentration.

Test Location Coupon Condition Findings

Test Location	**Coupon Condition**	**Observations**
Liquid space	Stressed	No general or localized corrosion, or SCC
Vapor space	Stressed	No general or localized corrosion, or SCC
Liquid space	Stress relieved	No general or localized corrosion, or SCC
Vapor space	Stress relieved	No general or localized corrosion, or SCC

B. Reaction mass with high ferric chloride concentration.

Test Location	**Coupon Condition**	**Observations**
Liquid space	Stressed	No general or localized corrosion, or SCC
Vapor space	Stressed	No general or localized corrosion. Severe SCC
Liquid space	Stress relieved	No general or localized corrosion, or SCC
Vapor space	Stress relieved	No general or localized corrosion, or SCC

Based on the success of the corrosion tests, economic studies were conducted. Results favored moving forward with zirconium for this service, but concerns remained. In particular, the people who had examined the original zirconium coupons, which had cracked into pieces, expressed a major concern over the possibility of a catastrophic failure in the event that SCC was not totally under control. The vessels in question contain hot, concentrated hydrochloric acid. The vessels are physically located above other operations and operating personnel. The downside of a catastrophic failure would be enormous. Although stress relieving the fabricated vessels would reduce the probability of SCC, concern remained. The use of clad construction, as contrasted to solid zirconium, was recommended to further address this concern. Even if SCC did develop, whether due to tensile stress formation and/or ferric chloride increases from upset conditions, failure of the zirconium cladding would not be any more catastrophic than the regularly occurring failure of existing glass-lined steel equipment. The fact that zirconium clad steel was considerably lower cost than solid zirconium was a bonus.

The potential of localized corrosion remained a possible concern. Although concentrations of ferric chlorides were expected to be low, high concentrations could potentially be encountered due to process upsets or other transient events. Because the application was considered to be pushing the envelope with regard to zirconium in an oxidizing HCl environment, Wah Chang proposed additional material processing precautions to assure a thick, stable oxide layer. These precautions focused on establishing a uniform zirconium oxide layer, which was considered vital to provide protection from ferric chlorides. This layer was obtained by thorough HNO_3/HF acid cleaning followed by a stress relieving and oxidizing heat treatment.

With major concerns addressed, safety and manufacturing reviews accepted zirconium as an alternative to glass-lined steel in this service. Initially, two zirconium 702 clad steel vessels were placed on order with AstroCosmos for an expansion project. These two vessels exceeded performance expectations and continue in service. From the Owner’s perspective they have proven successful from economical, safety, and environmental standpoints. Based on the success of the first two vessels; additional vessels and heat exchangers using zirconium clad construction were installed in similar service.

DESIGN, FABRICATION, AND TESTING

Vessel Description:

AstroCosmos, with strong team support from DMC and Wah Chang, fabricated two 2438 mm (96”) diameter zirconium clad carbon steel reactor vessels for this customer on a fast track basis. The success of these first two reactors lead to the fabrication of several additional zirconium clad reactor vessels. The Reactor shells and heads were fabricated from zirconium clad plates using 25mm (1”) nominal thick carbon steel, SA516 Grade 55. The reactor shells and bottom heads are externally jacketed with a conventional carbon steel jacket. The vessels incorporate a zirconium agitator and internal solid zirconium sidewall mounted baffles with baffle support gussets that are welded directly to the internal zirconium clad surface.

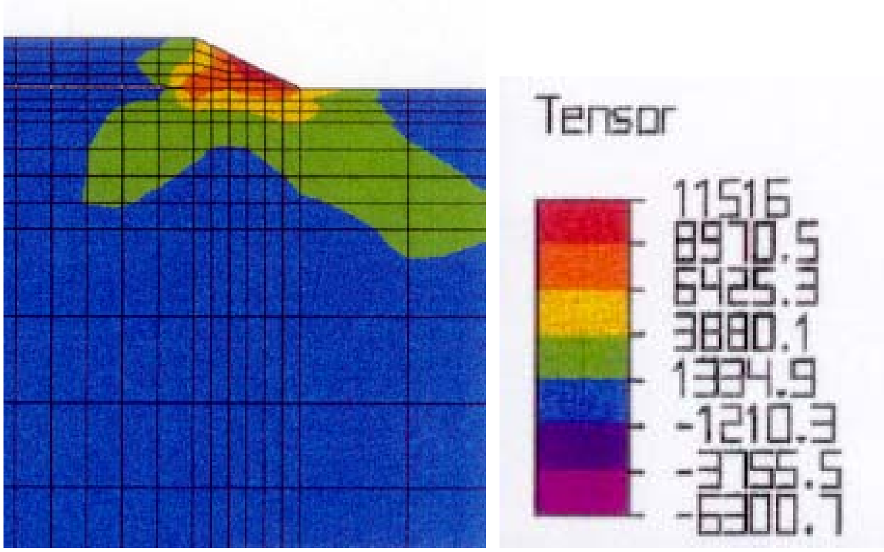
Zirconium Clad Vessel Design:

One of the major keys to the success of zirconium clad in this application was the careful consideration of a variety of design factors. Proper engineering of design features has a significant impact on the life expectancy of the vessels. Not only did the vessels need to meet ASME Section VIII Div.1, but they also had to satisfy a number of customer’s design requirements.

One requirement was that the vessels needed to be direct replacements for the existing glass lined vessels. The owner needed to be able to change over the vessels with a minimum of down time and to have the nozzle configuration match the existing piping. Clad fabrication does not have the same type of fabrication restrictions that limit glass vessels and therefore it is usually relatively easy to custom design and fabricate a clad vessel to match glass vessel configurations.

Another design element was to review all components to insure that the design was adequate for the severe pressure and temperature cycling that the vessels must endure. Finite Element Analysis was used to examine stresses in critical areas such as batten strap welds and jacket closure rings, Figure 1. Due to the high stress levels that the vessels would experience in operation, it was not enough just to engineer the weld joints for hydrotest pressures. Finite element analysis of standard batten weld joint designs revealed that stress levels, resulting from differential thermal expansion between zirconium and steel, were too high to provide the cyclic fatigue life that is required for these vessels. The coefficient of thermal expansion of zirconium is barely half that of carbon steel. This is a very critical fact to keep in mind when designing shell joints and nozzle connections. As a result, the size of the batten fillet welds was increased in order to reduce stress levels during operation, heat treatment and testing. Additional material data from Wah Chang allowed for a complete analysis of combined stresses due to thermal cycling, and pressure cycling between vacuum and high pressure.

Figure 1: A typical Finite Element Analysis presentation of stress patterns around a batten weld.

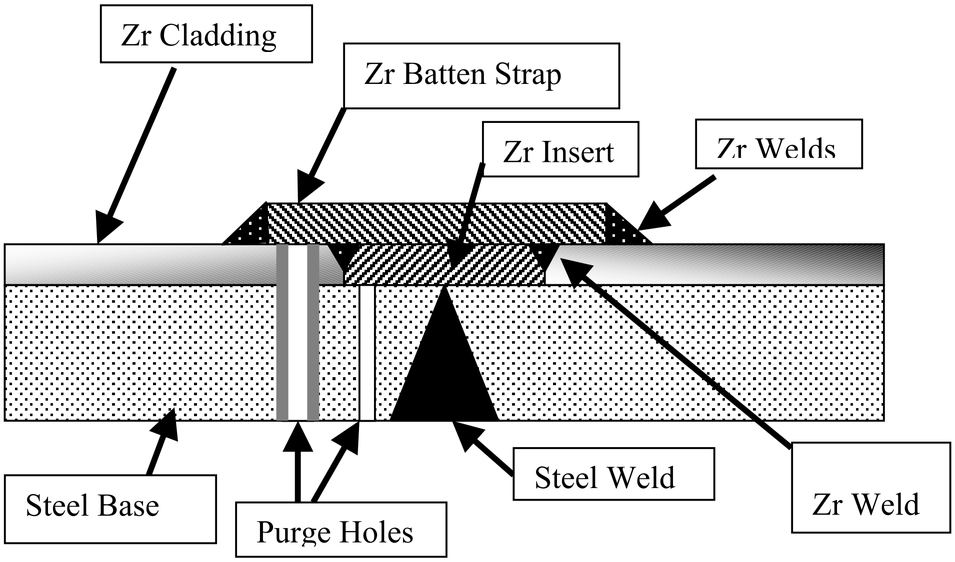


Extra corrosion protection for this application was provided by the incorporation of AstroCosmos' proprietary Dual Containment Batten System. The corrosive nature of the chemicals in these vessels is so severe that they would corrode through the steel vessel wall within days if the internal corrosion resistant zirconium liner were to fail. Standard clad construction incorporates a filler strip underneath the batten strap in order to replace the cladder that was stripped away in order to make the carbon steel weld joint. This filler is not necessarily the same material as the cladder, it can be copper or titanium for example. The AstroCosmos dual containment system uses Zirconium filler strips that are continuously welded to the adjacent zirconium clad surface. This continuous weld joint provides a second corrosion resistant barrier in case the primary batten strap weld fails. Extra care must be taken with the fit-up of this joint in order to insure that this joint will not crack or fail. The fit-up of the filler strip must be carefully controlled in order to provide a consistent root gap. This is critical in order to provide adequate weld penetration for strength, but not too much penetration, which would risk contamination of the zirconium filler strip weld with diluted carbon steel from melting of the backer plate. Figure 2 depicts a dual containment filler and batten strap joint.

Zirconium Clad Vessel Fabrication:

An important factor in reducing fabrication costs is to maximize the size of the clad plates in order to reduce the number of shell welds and batten strap joints. This was accomplished by splicing zirconium plates together prior to cladding. It is very important to maintain flatness of the zirconium sheets during and after the welding operation in order to avoid the possibility of cladding defects. The stand-off distance during cladding, which is a function of cladder flatness, is critical to the cladding process. Weld joint fit-up tolerances must be held tighter than ASME requirements in order to insure proper fit-up and welding of the filler strip joints.

Figure 2: Schematic of Dual Containment Batten-Strap Weld Design Concept



Cleanliness and adequate purging are always essential to good quality zirconium weld joints and zirconium batten strap welds are no exception. An adequate number of purge/test ports must be drilled through the shell and head weld joints in order to provide sufficient argon purging during the welding of filler strips and batten strap welds. Loose-lined and clad nozzle necks also require a minimum of two purge/test connections. All internal batten strap joint were welded with a minimum of two passes using the GTAW process as a means of providing sufficient weld area to resist design stresses.

Post weld stress relieving was accomplished in a gas fired furnace using a strict procedure to insure uniform temperature throughout the vessel and controlled heating and cooling rates. Prior to the stress relief heat treatment, the complete interior surfaces of the vessels were thoroughly cleaned and then acid washed with a HNO_3/HF solution to remove any final residual contamination.

To the best of our knowledge, these vessels are the first zirconium clad vessels to be heat treated after completion of internal zirconium weld joints.

Inspection and Testing:

Avoiding surface contamination of the zirconium cladding is critical for assuring effective corrosion performance later in service. Residual surface iron contamination must be removed before any high temperature operations. The plates were periodically checked for residual particles of iron on the surface. A salt spray procedure causes iron spots to display a highly visible brown rust stain. Any spots of iron surface contamination are removed by grinding and then rechecked as needed. The salt spray procedure has been found to be as effective as the more traditional ferroxyl test on zirconium and titanium, while being significantly more environmental friendly.

Ultrasonic testing was performed on the zirconium clad surface adjacent to the baffle gusset attachment welds and other spot areas to assure that the stresses of forming, welding and heat treatment had not caused any disbonding of the clad. No bond defects were detected in the vessels.

All zirconium welds were dye penetrant and helium leak tested prior to heat treating and after final hydrotesting. A measure of the high quality of welding fabrication was the fact that no filler or batten strap weld leaks were detected after heat treat and hydrotesting of the vessels.

Figure 3: A typical jacketed zirconium-steel clad pressure vessel.

CLAD MANUFACTURE, QUALITY ASSURANCE and PERFORMANCE CONCERNS

Explosion Clad Manufacture:

The zirconium-steel explosion clad materials used in construction of the vessels were manufactured by Dynamic Materials Corporation (DMC) at their Colorado explosion cladding facility. The details of the explosion cladding operations and technology are extensively presented in the referenced papers. (Ref. 1-4) Only the cladding operations and issues of specific interest for the manufacturing and quality assurance of the subject vessels are addressed here.

Each of the vessels required the manufacture of clad plates 2670 mm x 3650 mm x 30 mm (105" x 144" x 1.188") for the vessel side walls and two clad plates 3000 mm x 3000 mm (118" x 118") for the heads. Zirconium cladding sheets were 4.8 mm (0.188") thick.

The zirconium was compliant with SB551-702 with a further restriction of 1,000 ppm maximum oxygen content. The base metal was carbon steel, SA516 Grade 55N. No additional interlayer metals were used between the zirconium and steel. In development work performed in the decade prior to this project, DMC had determined that restricting the yield strength of the zirconium sheet to a level below that of SB551 was needed to assure optimum clad product properties when bonding zirconium direct to steel. Through agreement with Wah Chang, this was achieved by controlling oxygen content, an acceptance criteria which could be established at the ingot stage. The importance of component metal mechanical property control is discussed in detail in earlier papers. (Ref. 5,6)

The clad plate sizes needed for vessel fabrication exceeded the sizes of zirconium sheet immediately available for this fast track project. Consequently, DMC fabricated the larger zirconium cladder sheets by edge butt welding of two smaller zirconium sheets. Although this manufacturing route is not unique, it requires exceptional control of the zirconium welding technique to assure weld soundness, ductility, and flatness, as discussed above. After welding, and before explosion cladding, the zirconium welds were inspected by both penetrant (PT) and radiographic inspection.

After the explosion cladding operation the zirconium weld was again inspected by PT to assure that no damage had occurred during the explosive operation. The plates were ultrasonically inspected over 100% of the clad surface to detect any areas of lack of bonding. Bond shear strength tests were also performed to confirm bond strength. For these specific plates, there were no nonbond areas in the product area required for vessel fabrication. The bond shear strength ranged from 240 MPa to 310 MPa (35 ksi to 45 ksi).

Head Manufacture- The 2438 mm (96") ID 2:1 elliptical heads were formed from 3000 mm (118") OD clad blanks by hot pressing. The specific forming temperatures are critical to assure bond quality in the finished head. Zirconium-steel clad is typically formed in the 540° to 800°C (1000° to 1500°F) temperature range. Insufficient forming temperature can result in contour problems and bond separation. Excessive temperature will result in formation of brittle intermetallic compounds at the bondzone which fracture during forming, again resulting in bond separation. Control of furnace atmosphere, surface cleanliness, and tool cleanliness are critical to assure that the zirconium cladding is neither contaminated or damaged. After forming, the heads were ultrasonically inspected over 100% of the surface to detect disbonding. The pre-welds which been made in the zirconium sheet prior to cladding were again inspected by PT to confirm that the welds had not been affected by the forming operation. This assured the Owner that the clad bond quality, zirconium properties, and base metal properties meet their order requirements.

Surface Cleanliness and Protection: During all cladding and fabrication operations, it is critical to assure that the zirconium surface is protected from deleterious materials. This involves protection from weld spatter, torch cutting spatter, and situations which could embed iron particles into the zirconium surface. Upon completion of the cladding operations, the zirconium surfaces were cleaned by blasting with a silicon-free, iron-free grit product.

Other Zirconium-Steel Pressure Vessels: The clad manufacture and inspection aspects of this project are not unique, but standard for DMC's zirconium-steel clad pressure vessel plate. DMC and Detaclad have supplied material for fabrication of 22 pressure vessel type equipment since 1985. These vessels are discussed in detail in a prior Wah Chang Conference paper (Ref 7). To the best of our knowledge all of these pieces of equipment are still in service and have experienced no significant clad related problems.

CONCLUSION

Zirconium-steel clad reactors were constructed as replacements for problematic glass lined vessels for a highly aggressive, hydrochloric acid service application. Clad manufacture and fabrication procedures plus design engineering considerations were critical for technical and on-time project success. In one unique aspect, as the final fabrication step the fully fabricated vessels were given a stress relief heat treatment to prevent potential stress corrosion cracking problems known to occur in the process environment. From the Owner's perspective the vessels proved successful from economical, safety, environmental, and performance standpoints. Much of the success of this project was the result of a "team" effort that seized an opportunity, and eventuality benefited all parties involved, particularly the end user.

ACKNOWLEDGMENT

The authors wish to thank the Owner Company's lead project engineer for support throughout this program and for assistance in preparing and editing this paper. Regretfully, for business reasons he cannot be given explicit personal credit for his contributions.

REFERENCES

[1] Technical Bulletin: Nobelclad NT 200, "Explosion Bonding Process", DMC Nobelclad Div., Rivesaltes, France

[2] Banker, J.G. and Reineke, E.G., "Explosion Welding ", ASM Handbook, Vol.6, Welding, Brazing and Soldering, American Society for Materials, Materials Park, OH, 1993.

[3] Patterson, R.A., "Fundamentals of Explosion Welding", ASM Handbook, Vol.6, Welding, Brazing and Soldering, American Society for Materials, Materials Park, OH, 1993.

[4] Lafont, M.C., Masri, T. and Nobili A., " Recent Developments in Characterization of a Titanium-Steel Explosion Bond Interface", Reactive Metals in Corrosive Applications Conference Proceedings, J. Haygarth and J. Tosdale, Eds., Wah Chang, Albany, OR, 1997. Pg 89-98.

[5] Prothe, C.E., "Explosion Cladding for Zirconium Process Equipment: Update on the State of the Technology and Potential Advances", ", Zirconium/Organics Conference Proceedings, L. Duke and J. Tosdale, Eds., Wah Chang, Albany, OR, 1997.

[6] Nobili, A. and Banker, J.G., "Recent Developments in Zirconium-Steel Explosion Clad", Reactive Metals in Corrosive Applications Conference Proceedings, J. Haygarth and J. Tosdale, Eds., Wah Chang, Albany, OR, 1997. Pg 83-88.

[7] Banker, J.G. and Nobili, A., "Zirconium Explosion Clad for Cost Effective Process Equipment: Application, Design, Fabrication", Zirconium/Organics Conference Proceedings, L. Duke and J. Tosdale, Eds., Wah Chang, Albany, OR, 1997.