Recent developments in Zirconium-Steel Explosion Clad

Published in Proceedings 1999 Reactive Metals in Corrosive Applications Conference, Wah Chang, Sept 1999 pp 83-88

Authors : **A NOBILI**, Technical Manager, NOBELCLAD,
Espace Entreprise Méditerranée, 1 Allée A. NOBEL, 66600 Rivesaltes France
e-mail : nobel@smi-telecom.fr
Phone : 33 4 68 64 37 40
Fax : 33 4 68 64 26 83

J. BANKER, President, Clad Metal Products Inc
PO Box 11313, 5365 Spine Rd, Suite A2, Boulder, CO USA 80301
e-mail : cladinc@aol.com
Phone : 1 (303) 581-0621
Fax : 1 (303) 581-9481

Abstract :

Due to its superior corrosion resistance, zirconium is the material of choice for many aggressive chemical processes. Zirconium is used in pressure vessels, heat exchangers, columns, piping, etc.

Zirconium clad plates provide the excellent corrosion resistance of zirconium combined with the high mechanical properties and easy fabrication of steel base materials. Explosion cladding has been proven to be a reliable process for manufacture of zirconium clad products. Equipment fabrication methods are well developed. Zirconium clad equipment has demonstrated performance comparable to solid zirconium.

Clad manufacture is discussed, including size capabilities, material limitations, and product characteristics.

1/ Introduction

Since 1970, zirconium has been increasingly used in the construction of chemical process equipment. Zirconium production has gone up from 45 tons in 1970 to 680 tons in 1997. Zirconium clad shows similar trends. The first zirconium clad heat exchanger tubesheets were installed around 1970. Since 1980, more than 225 heat exchangers and 20 pressure vessels have been manufactured with zirconium clad plates. This demonstrates the acceptance of zirconium clad as a reliable industrial material.

Like titanium, zirconium presents excellent corrosion resistance in many acids and bases [1]. Zirconium performs well in many corrosive media including : acetic acid (65 %), sulfuric acid, sorbic acid, nitric acid, urea, etc. However, the capital cost of zirconium equipment is particularly high in comparison with most lower performance metal options. The benefit of zirconium is realized through reduced life cycle costs. The cost of many zirconium components can be reduced by the use of zirconium clad onto a lower cost base metal.

Only a thin layer of zirconium is required to provide corrosion protection. The base metal can be chosen for mechanical strength and/or for the corrosion conditions on the other side of the equipment. Figure 1 shows the comparative cost of solid zirconium vs. zirconium-steel clad plate. For vessel plates cost reductions become quite significant when the required thickness of solid zirconium is 12 mm or greater. For heat exchanger tubesheets, the savings are significant above 25 mm. The cost of fabrication is also reduced. Typically fabricators estimate that the cost of solid zirconium vessels is about 70 % for metals and 30 % for fabrication. The cost of clad fabrication is comparable; but the metal cost is lower. When vessels have external jackets, or half-pipe assemblies, the cost reduction is even more significant.

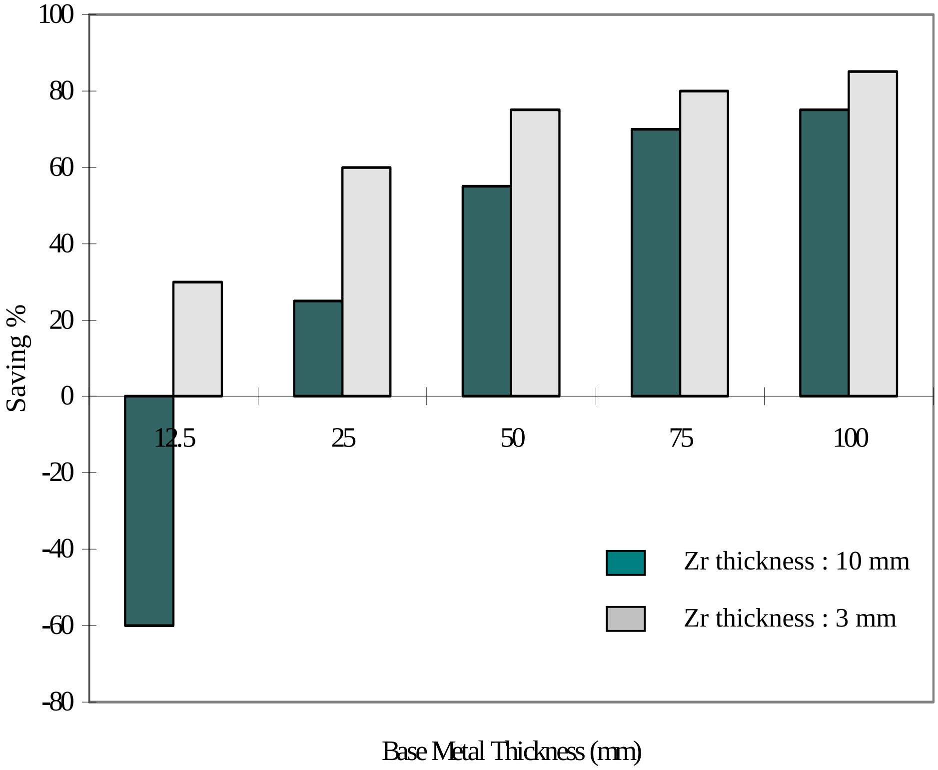

Figure 1 : Saving due to the use of clad plates instead of solid plates

Explosion cladding is the only proven technology for manufacture of zirconium-steel and zirconium-stainless steel clad plates.

2/ Explosion cladding process

The explosion cladding process was commercially developed during the early 1960's [2] [3]. Its usage has expanded continually over the subsequent years and currently stands at a world wide annual production total in excess of 10,000 tons. In 1996, 27,000 m² were produced.

Explosion cladding is a solid state joining process in which explosive energy is used to propel the component metals together under conditions which result in a metallurgical bond.

In practice, the clad and base components are spaced a small distance apart and explosive is placed upon the surface of the thinner component. Upon detonation of the explosive, the clad component, or flyer plate, is accelerated across the gap between the plates and collides with the base plate at an oblique angle. At the point of impact of the two components, thin surface layers are spalled off and are ejected from the region in the form of a jet. This jet of molten metal contains the surface contaminants which were originally present (typically oxides) that would otherwise prevent bonding. Upon collision, the two newly cleaned surfaces are driven into intimate contact under extreme pressure thus enabling the bond to be formed. Figure 2 presents a schematic of the explosion bonding operation.

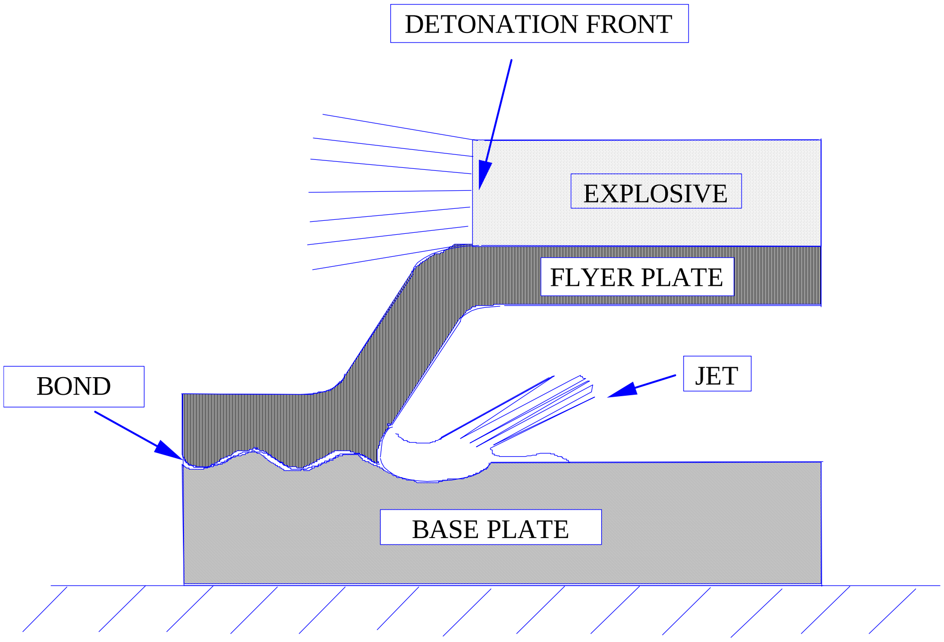

Figure 2 : Explosion cladding process schematic

Although the explosive detonation generates considerable heat, the rapid time scale of events and the considerable bulk of the metal, results in a minimal rise in the overall temperature of the metals. Due to this general absence of heating, the microstructure of the wrought parent metals and the associated mechanical properties and corrosion properties, remain essentially unaltered by the explosion cladding process. Due to the absence of any bulk heating of the wrought material, there are no heat affected zones.

The bonded interface is characterized by waves. Correct bonding parameters will control the morphology of these waves to avoid or minimize any continuous layer of melting or intermetallics. The resultant bond is tough, and comparable in strength to the weaker of the component metals. Excessive bonding energy can cause both melting and intermetallic formation, resulting is a brittle bond. Figure 3 shows a high quality bond interface between zirconium and steel.

Because of the lack of melting, properly manufactured explosion clad products do not exhibit many of the deleterious metallurgical characteristics of weld overlay clads. Further, unlike clad produced by rolling at high temperatures, the metallurgical characteristics of the parent materials remain essentially unchanged. The greater pressures involved and the lack of melting also allow metal combinations to be bonded that are not possible by these alternative methods.

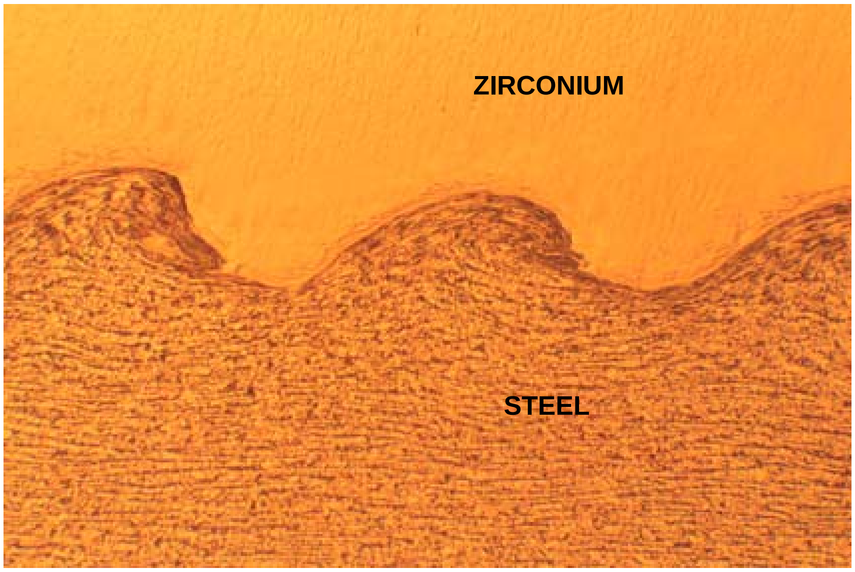

Figure 3 : Zirconium explosion clad plate interface

Table I shows a number of typical metal combinations that are produced by explosion cladding.

TABLE I : Some typical metals used for explosion clad plates

Cladder	**Base Metal**
Stainless steels 300 or 400 series Copper alloys Aluminum Nickel alloys Titanium Zirconium Tantalum	Rolled plates Carbon steels, A 516 Alloyed steels, A 387 Forged plates Carbon steels A 266, A 350 Alloyed steels A 182 Rolled and forged Stainless steels (300 series) Copper Aluminum

3/ Zirconium clad plates

3.1/ Manufacturing Limits- Component Metals

The explosion cladding process can be used to join zirconium to virtually any other metal. For some metal combinations, a thin interlayer between the zirconium and base metal improves bond quality and reduces cost. In production, the most common base metals are carbon steel and stainless steel. When cladding zirconium to steels, the best results are obtained when cladding moderate strength steels (i.e. ASTM A516 grades 55 to 70) with zirconium (ASTM SB 551 grade 702), having a yield strength no higher than 275 MPa. The zirconium yield strength is typically controlled by assuring that the oxygen content is below 1000 ppm, commonly referred to as “Low Ox”.

As the cladding metal strength and/or base metal strength increase above the values indicated above, bonding becomes more difficult. Further, as the cladding metal becomes thicker, bonding also becomes more difficult. In these cases an interlayer of pure titanium, typically 2 to 3 mm thick, is commonly used. Titanium is chosen because of its metallurgical characteristics, because there is no formation of brittle intermetallic compounds between zirconium and titanium, and because pure titanium bonds readily to steel over a broader production parameter range.

Nobelclad use a titanium interlayer when bonding zirconium to steels under the following guidelines:

- Zirconium, Low Ox, ≥ 10 mm thick
- Zirconium, not Low Ox, at all thicknesses
- Zirconium cladded onto stainless steel, whether Low Ox or not

Conversely, when cladding Low Ox zirconium to standard carbon steels, SA516 or similar, an interlayer is not used for zirconium thicknesses below 10 mm.

When an interlayer is needed, Nobelclad uses a proprietary technique to bond both the zirconium and the titanium in a single bonding operation. This minimizes costs and results in a superior bond.

The wave formation during bonding reduces the ductility of the zirconium. To restore the ductility a stress relieving heat treatment is generally carried out after bonding and before further processing. For zirconium-steel clad plates, the temperature of heat treatments are between 540 and 600 °C. This heat treatment reduces bond strength while improving toughness. Heat treatments at higher temperatures can reduce bond strength to unacceptable levels. Figure 4 presents the relationship between stress relief heat treatment temperature and bond shear strength.

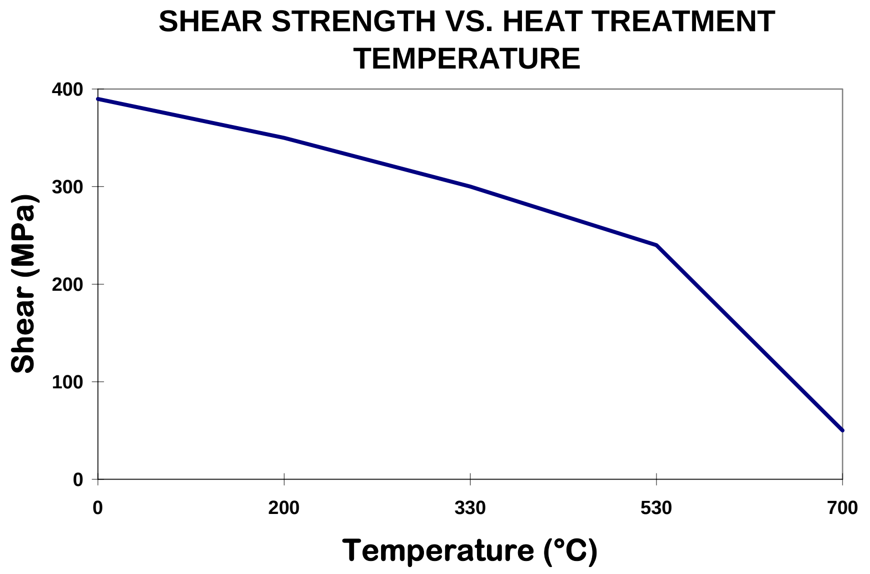

Figure 4 : Bond shear strength after 4 hours at temperature

3.2/ Manufacturing Limits- Size

The largest zirconium-steel clad plates that Nobelcad has produced at this time is 10 m² (110 sq-ft) in area. However, based upon prior experience with both titanium and zirconium, Nobelclad is gradually increasing production limits to those typical for titanium steel, Table II.

Typically the first constraint on clad plate size is the availability of the cladding metal sheet. By edge butt welding cladding metal sheets together, much larger clad plates are possible. This pre-welding technique has been used successfully with both titanium and zirconium for several years.

TABLE II : Production Size limits for Nobelclad titanium clad plates

	Standard Limits
Length (m)	10
Width (m)	4
Surface (m²)	30
Weigth (tonnes)	25
Cladder thickness (mm)	15
Base thickness (mm)	300

3.3/ Clad Product- Mechanical properties

Table III presents bond shear strength data from five production jobs performed between 1996 and 1998. The bond between the base metal and the zirconium, or the titanium interlayer when applicable, is consistently over 220 MPa (32,000 psi). When an interlayer is used, the strength of the zirconium-titanium bond is typically over 300 Mpa (43,000 psi).

3.4/ Clad Product- Specifications and Testing

ASTM Specification B898, “Standard Specification for Reactive and Refractory Metal Clad Plate” has recently been approved. This specification was developed by a world-wide team comprised of clad manufacturers, equipment fabricators, and equipment owners. It incorporates most of the requirements of earlier proprietary specifications. Prior to B898, zirconium clad was typically produced to either manufacturer or customer proprietary specifications, for example, Nobelclad NC501 or Rhom & Haas Specification 99062.

Integrity of the bond is determined by ultrasonic testing. Inspections normally conform to the procedures of ASTM A 578. Specification B898 UT Grade B, restricts any individual bond defect to 75 mm maximum length with total nonbond area not to exceed 97 %; UT Class A is tighter at 25mm and 99% respectively. Both Classes require inspection of 100% of the clad surface after completion of all relevant manufacturing operations.

The bond strength is usually measured using the bond shear strength test, ASTM B898 Figure 1. B898 and most other specifications impose 140 MPa (20,000 psi) minimum shear strength. Nobelclad average values exceed 250 Mpa in the stress relieved heat treated condition.

TABLE III : Characteristics of some typical Nobelclad zirconium clad plates

Job Number	**Number of plates**	**Base Metal**	**Zirconium Rp0,2 and Type**	**Thickness Base + Zr** (mm)**	**Length & Width (mm)**	**Shear test (MPa)***
96200	2	304L	150 MPa Low Ox	95 + 3 + 10	2080 x 2030	296/312
97103	5	A516 G55	196 Mpa Low Ox	71 + 4	3580 x 3100	240
98092	1	A516 G70	212 Mpa Low Ox	20 + 3	6270 x 1490	
98087	1	304L	193 Mpa Low Ox	8 + 3 + 10	2820 x 1480	
98160	4	A516 G70	395 Mpa Standard 702	100 + 3 + 10	2190 x 2190	380/280

* Shear tests are performed after heat treatment. Two values are shown for shots using a titanium interlayer. The first value is for titanium/zirconium bond. The second value is for Titanium/Steel bond.

** The presence of a middle number indicates that the part was shot with a titanium interlayer.

4/ Bond Characterization Study [8]

Nobelclad has recently performed a six month study with a french engineering school to analyze the interface of a zirconium clad plate and learn more about the bond. The complete contents of the 67 page thesis are not presented in this report. The full report is available from Noblelcad upon request. A summary of the report is as follows.

The zirconium/carbon steel bond was characterized in three material conditions:
Condition 1: As bonded
Condition 2: Condition 1 + plus a 540°C - 1 hour heat treatment
Condition 3: Condition 2 + standard surface finishing by grinding

X-ray image scanning analysis showed that no diffusion occurred between metals in any of the three conditions. It further showed that Zr-Fe intermetallics were present in the wave swirl and at isolated melt pockets on the back of the waves.

AFM (Atomic Force Microscopy) showed a perfect bond without any diffusion or transition region for all three conditions. Figure 5 shows a AFM presentation of the bondline. The zirconium is at the top of the picture. The steel at the bottom is recessed due to greater metal removal during specimen preparation. The bond is in the step-down region.

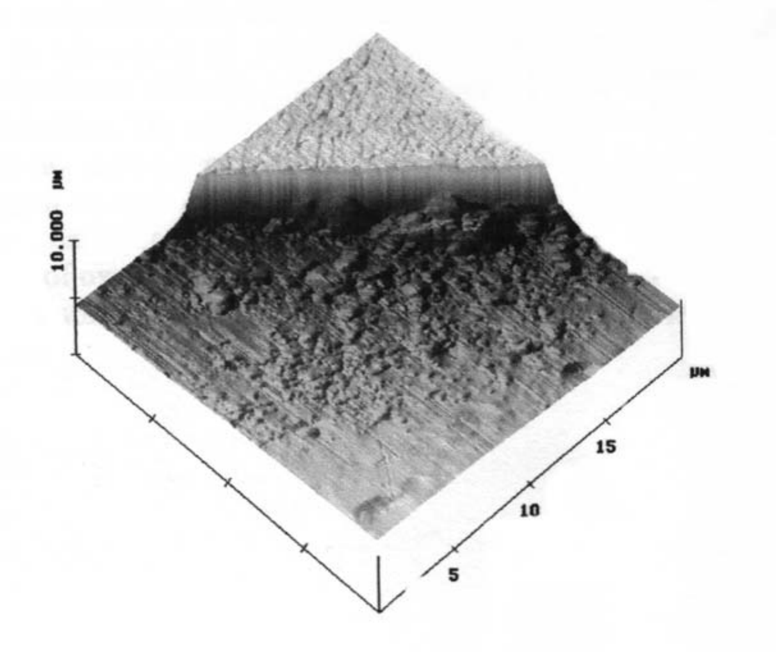

Figure 5: Atomic Force Microscopy of the zirconium-steel bond. Approximate scale: 1cm=1µm.

Microhardness scans showed a hardening of both zirconium and steel in a region approximately 10µm on each side of the interface. There was no appreciable change in hardness or microstucture further into the metals. Conditions 2 and 3 exhibit recrystallization of the zirconium, and reduction in microhardness, in the afore mentioned region. Partial recrystallazation of the steel in the cold worked region was observed with partial reduction of the hardness.

The oxygen content in the zirconium was not altered by the bonding operation, the heat treatment, or the final grinding operations.

The steel at the bondzone in Conditions 2 and 3 exhibits a residual tensile stress. The zirconium exhibits a residual compressive stress. These appear to be the result of the differential coeficients of thermal expansion as the metals cooled from the stress relief temperature.

Salt spray corrosion tests were performed on zirconium from all three conditions as well as with as-received zirconium. No changes in corrosion performance was observed.

5/ Clad plate use and fabrication [4] [5]

5.1/ Welding

Zirconium and steel cannot be fusion welded directly together because of formation of brittle intermetallic compounds. Consequently, weld joints between zirconium-steel clad plates are commonly made using the batten strap design concept shown in Figure 6. About 12 mm of zirconium are removed on the edges to be welded. The steel base metal is prepared and welded according to usual steel fabrication procedures (V or X groove). A UT is then generally recommended. An insert (silver, titanium, copper or zirconium) is put in the space where the zirconium was removed (brazed, tack welded, or left unattached) ; the zirconium batten strap is then welded over the top. Adequate shielding (including root and trailing shields) of the molten pool and adjacent areas must be provided to avoid oxygen contamination which cause embrittlement. As with all zirconium welding, cleanliness is critical.

A stress relieving heat treatment may be carried out after welding operations to improve corrosion performance in some environments; a common temperature is 425 °C .

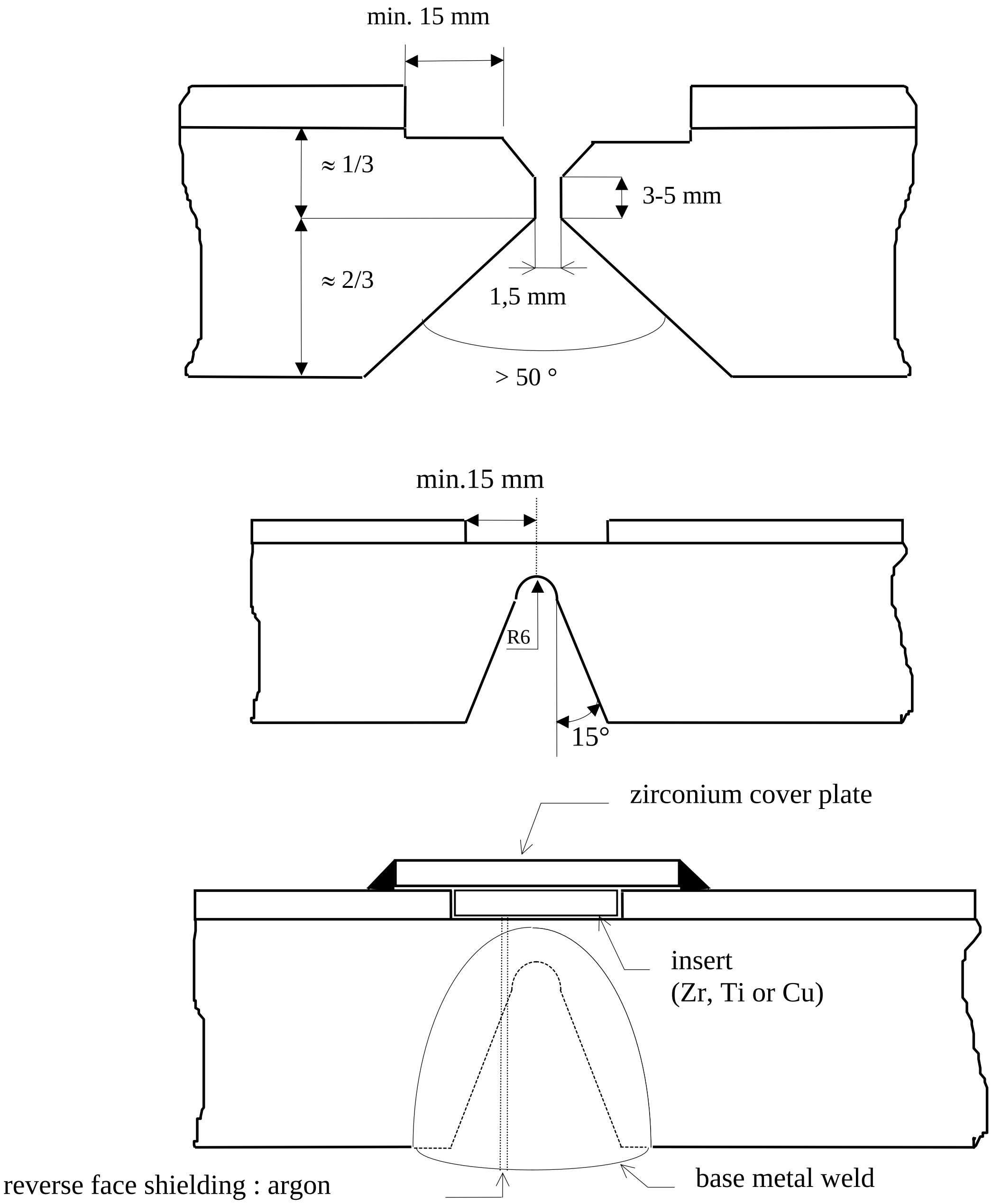

Figure 6 : Batten Strap Concept for welding of zirconium-steel clad plates

5.2/ Forming

Zirconium clad plates can be cold or warm formed. Warm forming temperatures are about 500-600°C. Heads (up to 2.8 m diameter) have been successfully warm pressed. Larger heads have been constructed from formed segments.

5.3/ Cutting

Zirconium clad plates can be cut by any regular means (sawing, water jet, flame cutting, plasma cutting) with proper precautions: begin with the zirconium face and avoid significant interface overheating.

5.4/ Machining

General recommendations for machining are to use low cutting speeds and maintain a high feed; to use liquid coolant abundantly; and to use only machines with adequate power and correct clamping.

Overheating during drilling to be avoided in that it can cause sufficient stresses to result in disbonding. Recommendations are :

- to begin drilling from the zirconium face,
- to change drilling speed as it passes from one metal to the other,
- to use carbide tipped drills,
- to keep drills sharp.

Drilling of several clad plates at the same time is not recommended.

5.5/ Main applications [4] [6] [7]

The primary commercial applications of zirconium clad plates are tubesheets for heat exchangers and plates for pressure vessel construction. Some specific applications include:

Heat exchanger tubesheets for methlymethacrylate process
Heat exchanger tubesheets for nitric acid cooler condensers
Reactors for acetic acid manufacture
Columns for processing of organic acids
Rotary kiln for zirconium oxide manufacture

Tubesheets have been manufactured up to 2.3 m diameter with steel thickness of 100 mm and zirconium cladding of 10 mm thick. Base metal is carbon steel (ASTM A 516 Grade 70 or 55) in about 75 % of the applications and stainless steel (304L or 316L type) in the balance.

Pressure vessel plates as large as 2.92 m x 3.45 m have been supplied to fabricators. For vessel plates, zirconium thickness is typically 3 to 4.8 mm.

6/ Conclusion

Zirconium clad plates combine corrosion resistance of the cladder metal with mechanical properties and low cost of the base metal. Over fifteen years performance of clad pressure vessels and heat exchangers have demonstrated their commercial and technical viability. The explosion cladding process is proven to produce clad plates with a consistent high quality level. Clad fabrication techniques are well developed and well proven.

References :

[1] TRICOT Roland, CEZUS, “Le zirconium dans le génie chimique, caractères principaux de la construction chaudronnée”, Matériaux et Techniques, Avril - Mai 1995.

[2] PATTERSON R.A., “Fundamentals of Explosion Welding”, ASM Handbook, Vol.6, Welding, Brazing and Soldering, American Society for Materials, Materials Park, OH, 1993.

[3] BANKER J.G. & REINEKE E.G., “Explosion Welding “, ASM Handbook, Vol.6, Welding, Brazing and Soldering, American Society for Materials, Materials Park, OH, 1993.

[4] BANKER J.G., “Commercial Application of Zirconium Explosion Clad”, Journal of Testing and Evaluation, JTEVA, Vol. 24 No.2, pp. 91-95, American Society for Testing and Materials, Philadelphia, March 1996.

[5] CABROL J.C., MOINARD P., GAGNEPAIN J.C., DUPOIRON F., JOBARD D., CHARLES J., “Tôles zirconium massives ou plaquées : propriétés d’emploi et de mise en oeuvre”, *Journées zirconium*, 1995

[6] BANKER J.G. & NOBILI A., “Zirconium Explosion Clad for Cost Effective Process Equipment : Application, Design, Fabrication”, Zirconiu/Organics Conference Proceedings, L. Duke and J. Tosdale, Eds., Wah Chang, Albany, OR, 1997.

[7] YAU, T., “Zirconium in Cooler Condensers for Nitric Acid”, Stainless Steel World, Zupten, the Netherlands, Sept. 1996.

[8] GUSTAFSSON J, "Characterization of a clad plate Zr/steel. The clad plates influence on the interfacial metallurgical quality", currently unpublished, 1999.

Recent Developments in Zirconium-Steel Explosion Clad

Authors : A. NOBILI
J. BANKER

Key words :

Explosion Cladding / Zirconium / Clad plates / Zirconium clad