NobelClad™

RECENT ADVANCEMENTS IN TITANIUM AND ZIRCONIUM CLADDING TECHNOLOGY

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A DMC Global Company™

AGENDA

- Explosion Cladding Overview
- Ti & Zr Explosion Clad Developments
- Enhanced Corrosion Resistance of Zr Clad

Section 1

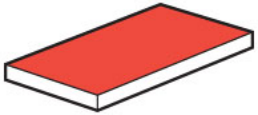
Titanium & Zirconium Explosion Cladding Overview

NOBELCLAD TODAY

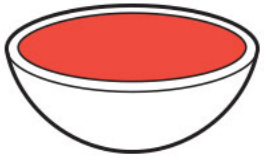
- Most advanced explosion clad technology worldwide since 1962
- High reputation for **reliability**, **service** and **product quality** worldwide
- Published over 80 papers on explosion cladding process, applications and markets
- Research & development departments in each production site
- Metallurgists and welding engineers support projects

TI & ZR EXPLOSION CLAD PRODUCTS

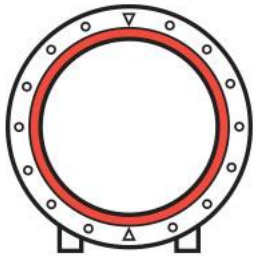
Plate Products



PLATES



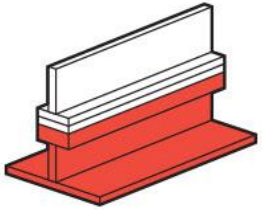
HEADS



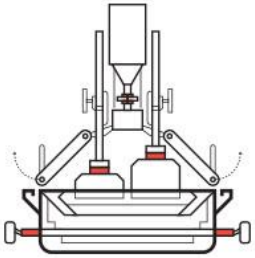
SHELLS

TUBESHEETS

Transition Joints



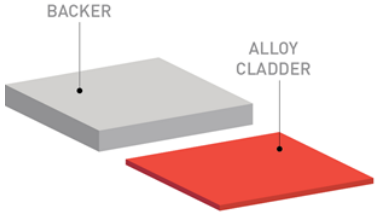
STRUCTURAL



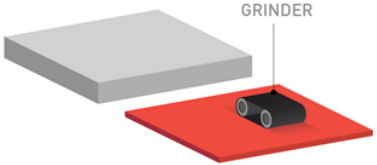
ELECTRICAL

CRYOGENIC

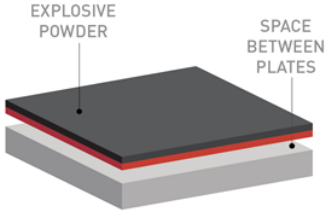
TI & ZR EXPLOSION CLAD PROCESS



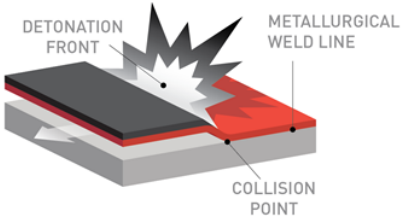
1. PLAIN MATERIAL INSPECTION



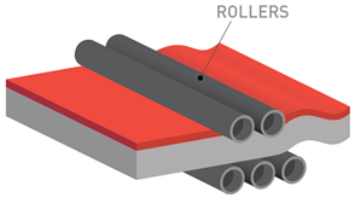
2. GRIND MATING SURFACES



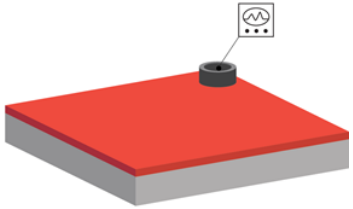
3. ASSEMBLE BACKER, CLADDER & EXPLOSIVE



4. EXPLOSION



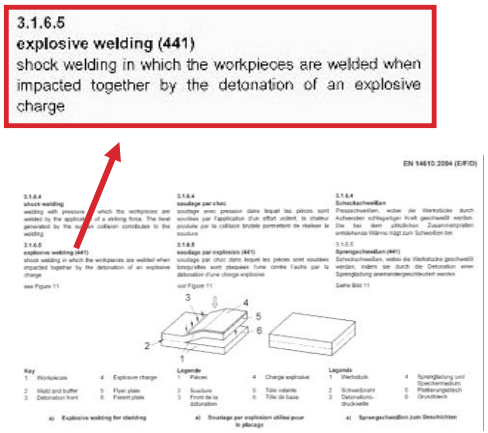
5. FLATTENING & CUTTING

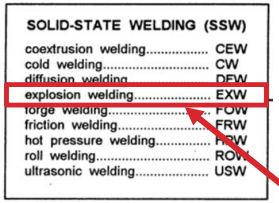


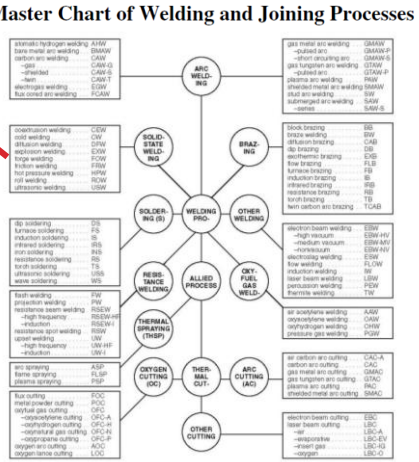
6. TESTING & INSPECTION

EXPLOSION WELDING CLASSIFICATION

- Process developed, commercialized and standardized in the 1960's and classified in **EN 14610, EN ISO 4063** and American Welding Society **(AWS) WHC3.09**

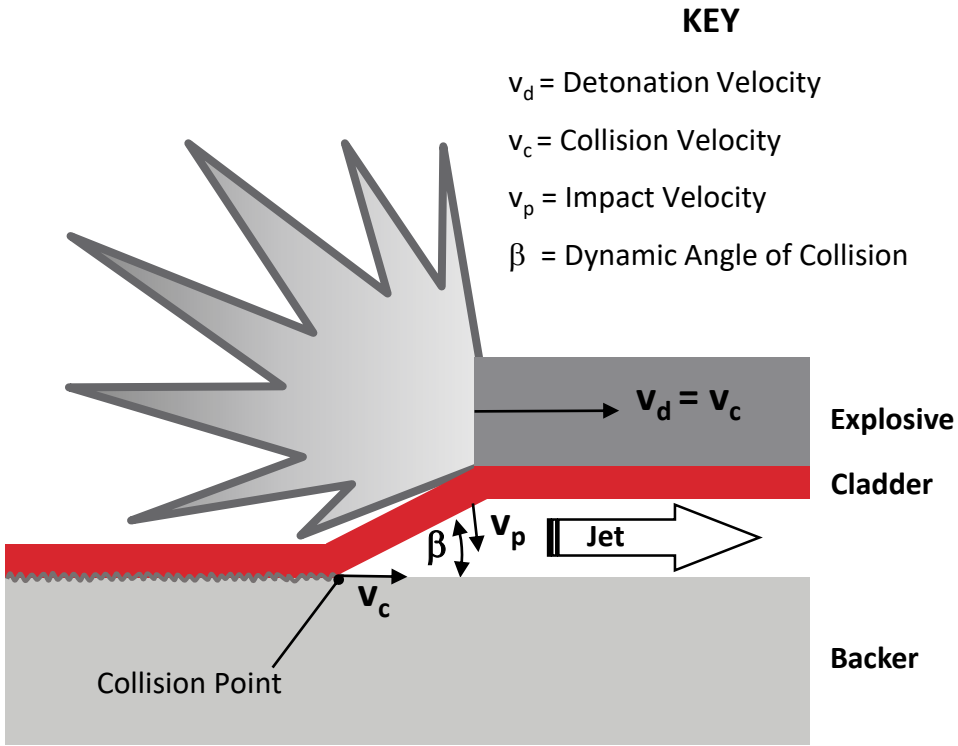




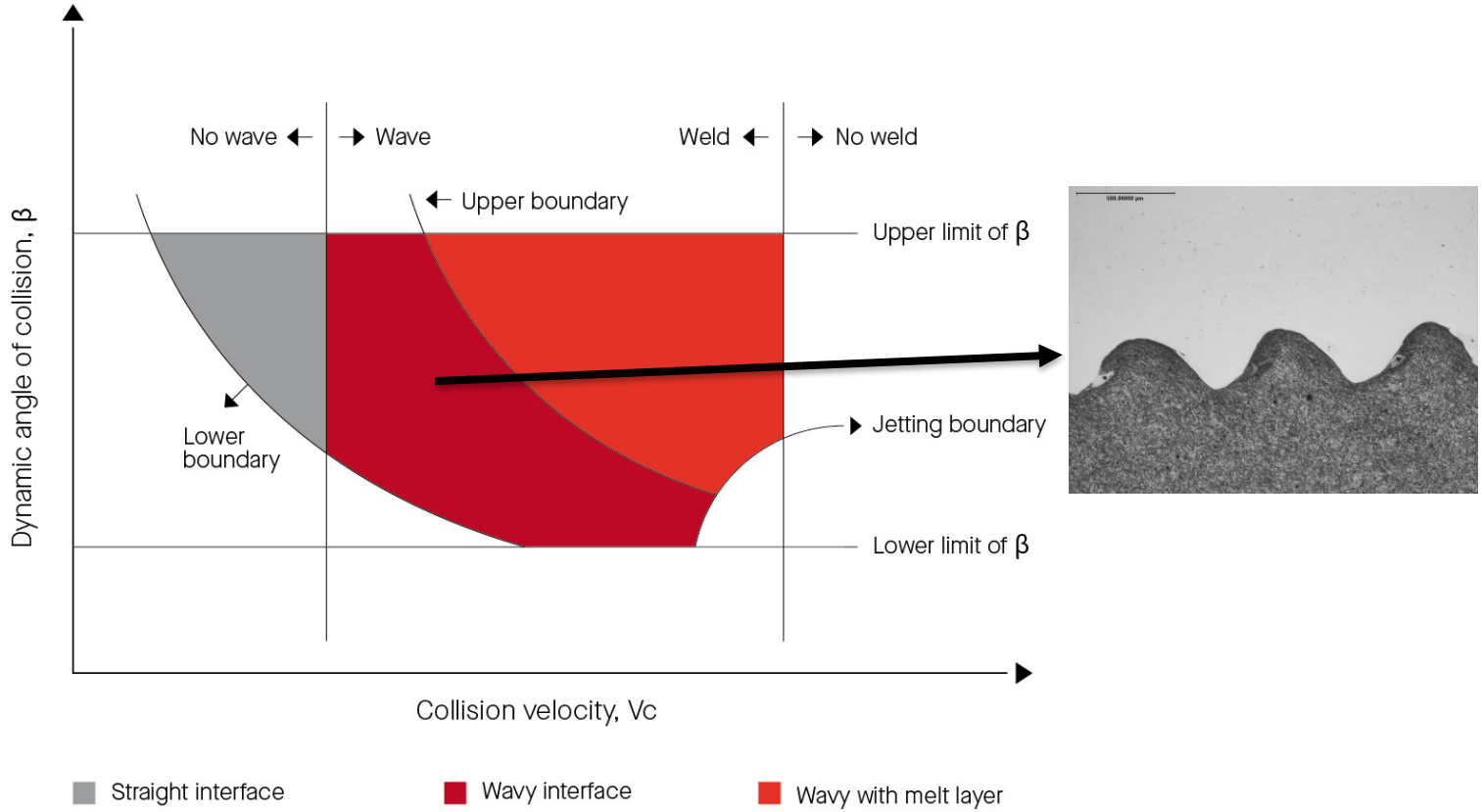


EXPLOSION CLADDING PARAMETERS

- Key Process Parameters
  - Input material meets specifications
  - Careful preparation and assembly
  - Final inspection
- Unique parameters for > 300 metal cladding combinations

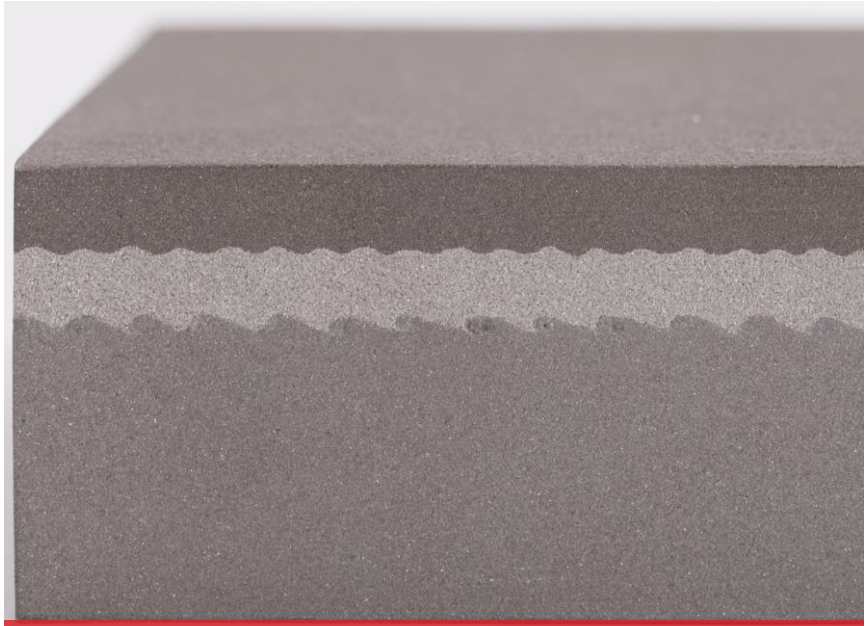


EXW PROCESS CONTROL - WELDING WINDOW



BENEFITS OF CLADDING UNDER OPEN AIR

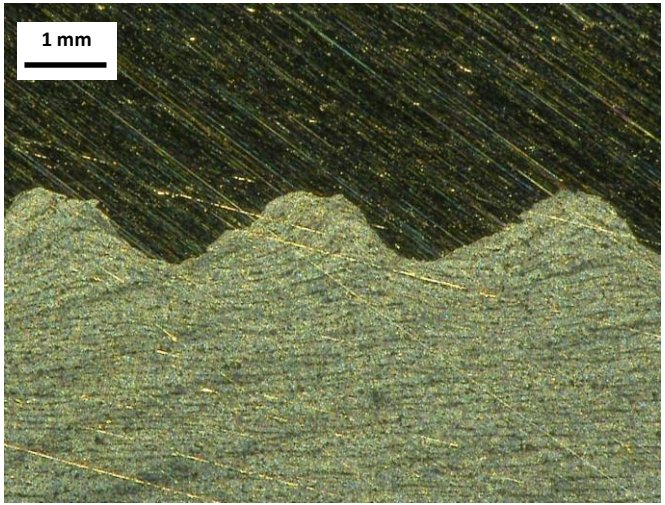
- Cladding with high energy yields significantly larger clad plates sizes and clad thicknesses vs. vacuum cladding and other methods.
- The wave structure obtained from high energy bonding produces a higher bond strength across the clad plates providing higher protection from disbonding during:
  - Plate rolling & welding
  - Head forming & welding
  - Tubesheet drilling
  - Tube-to-tubesheet welding
  - Equipment operation & weld repairing
- ***High energy bonding in underground open-air chambers is used to achieve the highest bond strength and produce the largest plates commercially available.***



Explosion cladding :
High Energy Clad = Wavy Interface = High Bond Strength

EXPLOSION CLADDING - PROS & CONS

- Advantages of Explosion Cladding
  - Solid state welding process = No dilution, No HAZ
  - Offers full compliance with chemical and metallurgical requirements of Cladding and Base metal specifications
  - Corrosion performance is not affected by the cladding process
  - Corrosion allowance not needed for Ti & Zr clad
- Disadvantages of Explosion Cladding
  - Construction of clad vessels requires expertise due to complexities of attaching nozzles, internals, or attachments
  - Cladding complex geometries is difficult
  - Cladding cannot be used for field repairs



Section 2

Titanium & Zirconium Clad Developments

- Common & Emerging Clad Applications
- Increased Size of Clad Plate & Clad Heads
- New Material Combinations - Duplex SS Base Metal

COMMON GRADES OF REACTIVE METALS FOR CLADDING

Can Be Direct Clad (1 Layer)

		UNS #
• **Ti Gr. 1**	Commercially pure, low oxygen – *stock item*	R50250
• **Ti Gr. 11**	Titanium - 0.2% Palladium alloy, low oxygen	R52250
• **Ti Gr. 17**	Titanium - 0.05% Palladium alloy, low oxygen	R52252
• **Zr700**	Commercially Pure Zirconium, low oxygen	R60700
• **Ta**	Tantalum Unalloyed, from ingot	R05200

Interlayer Needed (2 Layers)

• **Ti Gr. 2**	Commercially Pure Titanium	R50400
• **Ti Gr. 7**	Titanium - 0.2% Palladium alloy	R52400
• **Ti Gr. 16**	Titanium - 0.05% Palladium alloy	R52402
• **Zr702**	Commercially Pure Zirconium	R60702
• **Ta2.5W**	Tantalum - 2.5% Tungsten Alloy	R05252

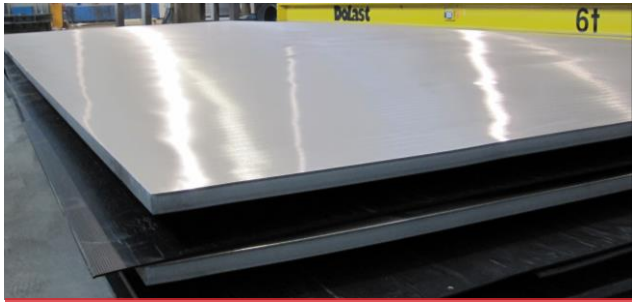
Zr702 with Ti Gr. 1 Interlayer

DETACLAD® RANGE OF CAPABILITIES

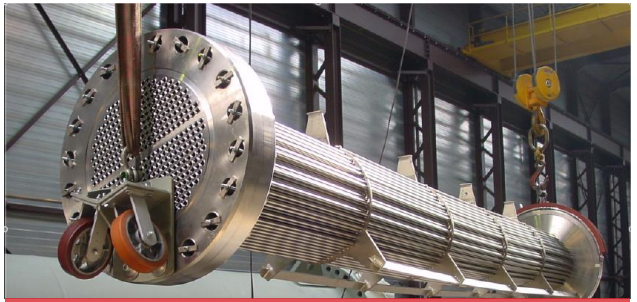
- Base thickness: 1 mm to 1000 mm -> *or thicker depending on local shipping weight restrictions*
- Width: 5 m max
- Length: 15 m max
- Weight: 50 tons max
- Cladding thickness: 1 mm to 35 mm
  - Up to 18mm for Titanium
  - Up to 12mm for Zirconium

Reactive Metal Clad Plates - Maximum Size (on carbon steel)

Ti Gr. 1, 11, 17	4m x 8m
Zr 700	4m x 6.6m
Zr702 (w/interlayer)	2.4m x 3.7m
Tantalum, Niobium	2m x 3m



DETACLAD™ PLATES



DETACLAD™ TUBESHEETS

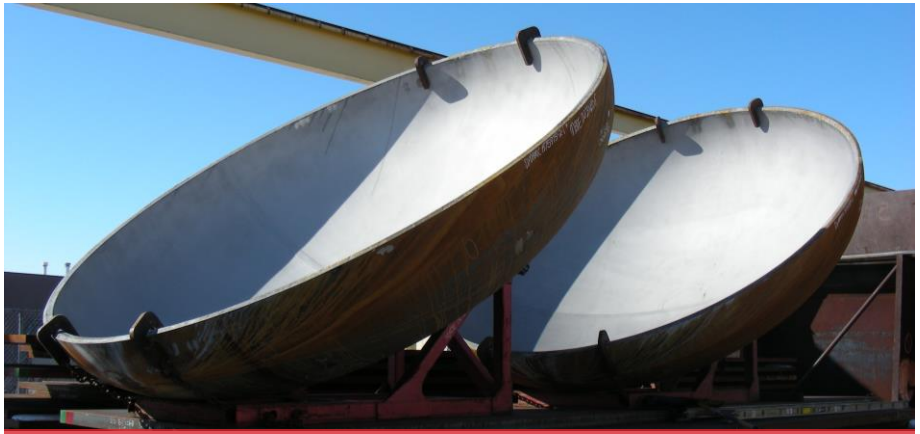
CLAD HEAD FABRICATION

- Titanium and Zirconium clad plates can be formed into cans or heads by either cold or hot forming, dependent upon fabricator equipment forming capabilities.
- Depending on available plates size and size/geometry of heads, segmental construction may be necessary for head forming.

Welded Segmental Clad Head

TITANIUM & ZIRCONIUM – CLAD FORMED HEADS

- Diameters: Up to 5m (Ti or Zr clad)
- Clad Alloy Thickness: 2 to 12 mm
- Base Metal Thickness: 10 mm or thicker
- Clad ‘pre-welds’ comply with ASME Code requirements
- Large single piece clad heads offer significantly reduced # of welds in fabricated vessels vs. solid construction
  - Cost & lead time savings
  - Reduced inspections
  - Enhanced reliability



LARGE SINGLE-PIECE ZIRCONIUM CLAD HEADS

TI & ZR CLAD FOR CHEMICAL APPLICATIONS

Titanium & Zirconium cladding is commonly an economic solution for fabricated equipment including:

- Reactors
- Crystallizers
- Autoclaves
- Columns
- Large Tanks
- Tubesheets
- High Pressure Piping

EQUIPMENT BUILT FROM NOBELCLAD CLAD PLATES.

COMMON APPLICATIONS FOR TITANIUM CLADDING

1. Purified Terephthalic Acid (PTA) equipment – *largest application in CPI*
2. HPAL or POX Autoclaves - mining / hydrometallurgy
3. Nitric Acid Cooler-Condensers - fertilizer production
4. Urea Strippers - fertilizer production
5. Ethylene Dichloride (EDC) / Vinyl Chloride Monomer (VCM)
6. Epichlorohydrin (ECH)
7. Bioethanol – Reactors
8. Water Treatment – Ultrapure and Zero Liquid Discharge systems
9. Power Generation – condenser tubesheets
10. Desalination – heat exchanger tubesheets

TITANIUM CLAD VESSELS – PTA

- Purified Terephthalic Acid (PTA) Oxidation Reactors and Columns
- Operating Conditions
  - Powerful oxidizing acid at low pH
  - High pressure, 22 Bars
  - High temperature, 250º C (480º F)
- Reactor sizes up to 12m diameter, 75m long, 130mm thick
- Heat exchangers, tubesheets 200mm thick

Equipment Examples

Pictures provided by COEK Engineering

TITANIUM CLAD AUTOCLAVES

- Pressure Acid Leaching of Nickel and Cobalt
  - Temperatures to 275° C (525° F)
  - Pressures to 75 Bars
  - Sizes to 5m diameter, 35m long
- Pressure Oxidation Leaching of Gold and Copper

COMMON APPLICATIONS FOR ZIRCONIUM CLADDING

- Acetic Acid – *most common in CPI*
- Bioreactors
- Chlorinated Polyethylene (CPE)
- Ammonium Nitrate (AN)
- Cellulosic Ethanol
- Epichlorohydrin (ECH)
- Formic Acid
- Herbicides
- Methyl Methacrylate (MMA)
- Nitric Acid (HNO3)
- Pharmaceutical Reactors –> pH 0 to 14
- Polyphenylene Sulfide (PPS)
- Polyoxymethylene (POM)
- Propylene oxide (PO)
- Sulfuric Acid, 40-70% conc, above boiling
- Urea / Ammonium Carbamate

ZIRCONIUM CLAD - EXAMPLE

- High Pressure Urea Strippers
- Up to 2.75m diameter vessels
- Zr clad tubesheets, ~ 0.5m thick

SNAMPROGHETTI Zirconium Urea Stripper - *Courtesy of Luigi Resta*

ZIRCONIUM CLADDING – USED IN FIGHT AGAINST COVID-19

- **Methyl Methacrylate (MMA)—**a critical building block for Polymethyl Methacrylate (PMMA), the material used to make sheets of “plexiglass” or acrylic used for clear protective barriers
- Many of today’s MMA production facilities incorporate zirconium clad equipment
  - For acetone cyanohydrin (ACH) route
  - Many projects planned or underway
- Zirconium’s properties make it ideal for:
  - Hot, concentrated sulfuric acid resistance
  - Cost-effective clad columns and clad heat exchanger tubesheets

- Traditional Zirconium cladding techniques used titanium interlayer between zirconium & carbon steel (1960's)
- Direct bonding of zirconium to carbon steel developed by modifying the cladding process parameters and zirconium mechanical properties (1980's)
- Zirconium clad plates are commonly provided in two configurations:
  - **Zr700 direct clad to base metal (2-layer):** generally the most economical option allowing for the largest plate sizes and the shortest lead time
  - **Zr702 clad to base metal with a Ti Gr1 interlayer (3-layer):** for equipment that requires > 9.5mm (3/8") thick zirconium cladding, e.g., heat exchanger tubesheets

CAN TITANIUM OR ZIRCONIUM BE CLAD TO DUPLEX STAINLESS STEEL?

The lower nickel and molybdenum content of duplex stainless steels results in higher strength than 304 or 316 SS with similar or slightly better corrosion resistance. Additionally, in high purity water applications, duplex does not leach metals into cooling water.

Examples of Ti or Zr clad to Duplex Stainless Steel base metal:

- Nitrogen Fertilizer Plant Heat Exchanger
  - Zr702 clad to 2205 SS
- Ethylene Dichloride (EDC) Reactor
  - Ti Gr1 clad to 2205 SS
- Ultrapure Water Treatment for Semiconductor Manufacturer
  - Ti Gr12 clad to 2205 SS
- Marine Application
  - Ti Gr1 clad to 2507 SS

CLAD TUBESHEET IN MT. BRADDOCK, PA FACILITY

ZIRCONIUM CLADDING - SUMMARY

Zirconium Cladding is only available via the Explosion Welding (EXW) and not by Roll Bonding or Weld Overlay

Explosion welded (EXW) zirconium maintains the corrosion properties of the zirconium sheet

Commercially Pure (CP) grades of Zirconium, including the Zr700 and Zr702, can be clad to carbon steels, alloy steels, stainless steels, aluminum alloys, copper alloys, titanium alloys, nickel alloys and other backing materials

Explosion welding (EXW) allows for production of identical size plates for large projects as well as custom sized plates in small quantities for special needs

ZIRCONIUM CLADDING - SUMMARY

Plates can be clad on both sides with Zirconium when there is a need for inside and outside corrosion protection.

Single piece formed heads of clad zirconium can be produced

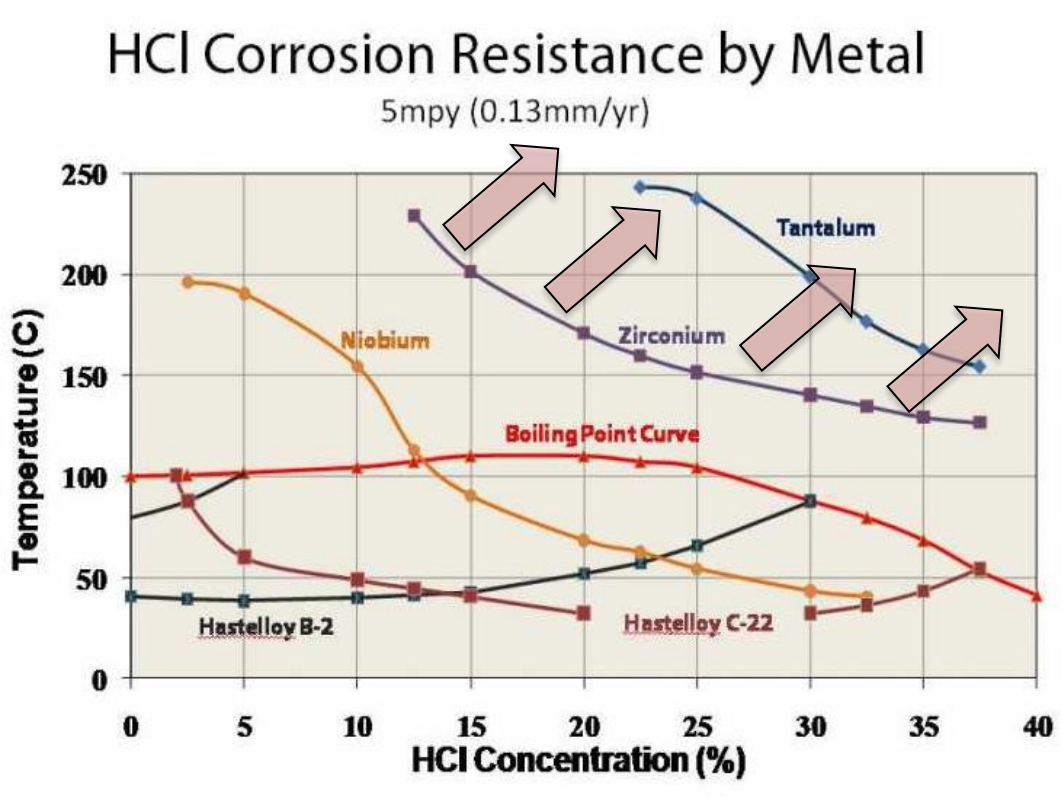
Multi-layer clad plates can be produced for transitioning from Zirconium to challenging alloys such as duplex stainless steel for tubesheets and related equipment.

Section 3

Enhancing the Corrosion Resistance of Zr Clad Equipment

CORROSION RATES IN HYDROCHLORIC ACID – ISO CORROSION DATA

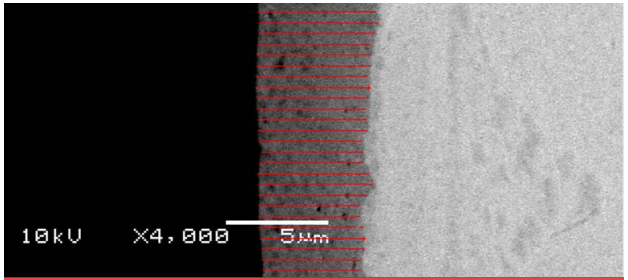
- Zirconium with Thermal Oxide treatment
  - Significantly improves corrosion resistance vs. non-treated Zirconium
  - Resists hot concentrated Hydrochloric Acid
    - Up to 36% HCl
    - 600 F (315C)
    - 1000 ppm Fe3+



ZIRCONIUM EQUIPMENT – THERMAL OXIDE - BENEFITS

- Zr702 oxide thickening treatment provides:
  - Reduced susceptibility to stress-corrosion cracking (SCC) by formation of an adherent oxide layer that exhibits compressive stress.
  - Enhanced corrosion resistance, especially in HCl with oxidizing impurities like ferric ions.
  - Improved resistance to erosion-corrosion, abrasion, galling, and wear.
  - Eliminates galvanic coupling, especially when Zirconium oxide (ZrO_2) thickness is 4-6 microns thick.

NOBLEIZING-R™ SURFACE TREATMENT ON ZR702: ENHANCES SURFACE HARDNESS, WEAR RESISTANCE
Courtesy of Flowserve Corp



CROSS-SECTION OF ZR702 SHEET SAMPLE (SEM), AIR OXIDIZED AT 610C FOR 24 HRS

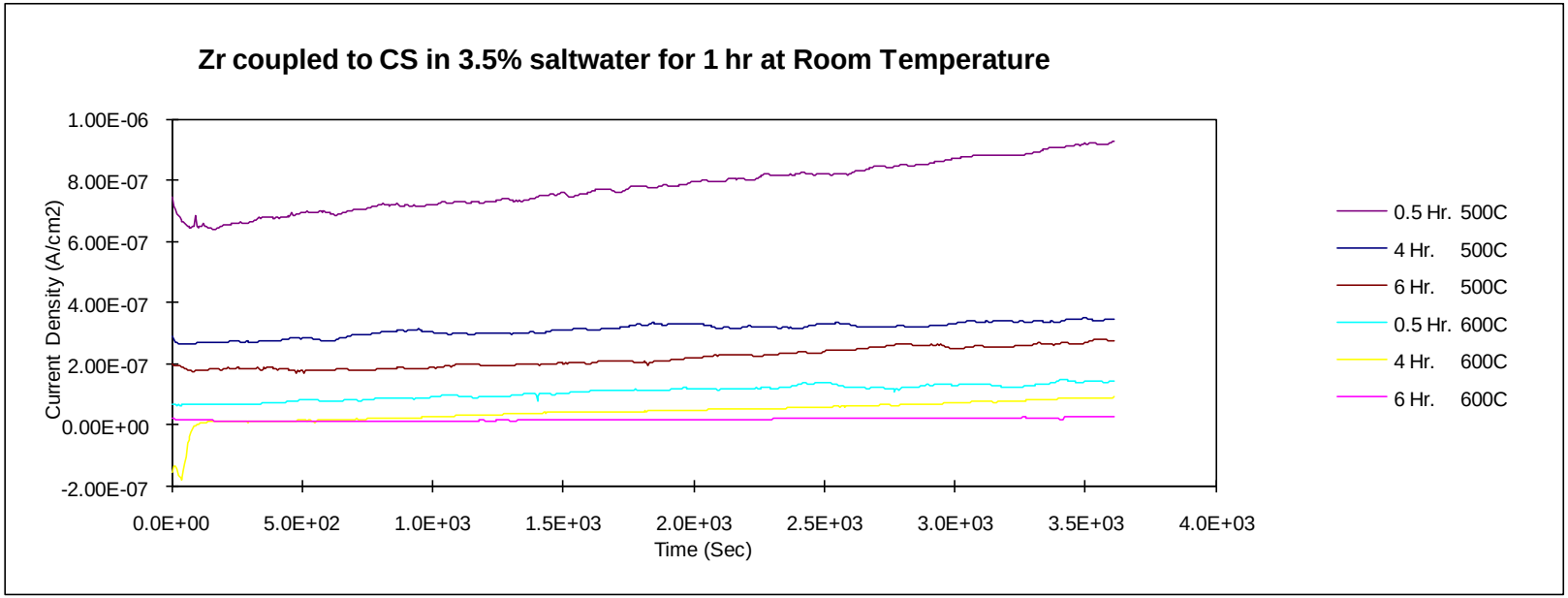
ZIRCONIUM EQUIPMENT – THERMAL OXIDE – CURRENT USES

- Tanks and pressure vessels
  - Solid or clad
- Agitator shafts and blades
- Trays and tray clips
- Fasteners and washers
  - Including dissimilar metal applications
- Pump and valve components

Zr700 Clad Reactor
'Thermal Oxide' Treatment
Courtesy of Mersen USA

GALVANIC COUPLING STUDY: 1:1 SURFACE AREA RATIO (ZR702:1020 CARBON STEEL)

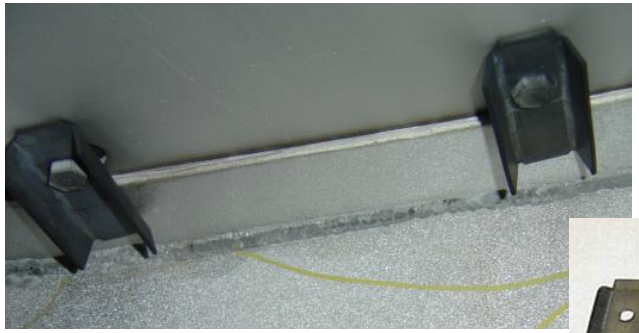
- Key conclusion: Galvanic couple broken – Zr702 Thermal Oxide treated @ 600C, 6 hrs



GALVANIC CORROSION IN SEAWATER VS. ZR702 OXIDE THICKNESS

- Electrochemical testing performed by ATI SAIC (Millersburg, OR) Corrosion Laboratory
- Examined galvanic couple with steel in seawater as a function of increasing oxide thickness
- Comparison of Zr702 mill condition vs. 500C & 600C oxide thickening air anneal
  - 3.5% seawater at ambient temperature
  - 1:1 surface area ratio with carbon steel
  - 0.5 hrs, 4 hrs, 6 hrs
- Galvanic couple reduced to nil after 600C / 6 hrs air anneal
  - Equates to oxide thickness of **2.5-3.0 um**

Zr Clips Fastened with Zr Bolts to 304L SS Tray Column



Qualifying Zirconium with Thermal Oxide Treatment

- Always validate performance with corrosion testing
- Welded corrosion coupons available

Courtesy of United Titanium

THANK YOU

Contact

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