DetaClad™ Characterization for High–Temperature and High–Pressure Hydrogen Service

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ABSTRACT

When it comes to considering high temperature damage mechanisms, one of the most challenging decisions is related to heavy-wall pressure vessels that operate at high pressure and high temperature in a hydrogen containing environment. Hydrotreatment or hydrocracking reactors typically fall under this category and often have an austenitic stainless-steel lining to protect the inner side of the pressure vessel from corrosion. Embrittlement of the carbon steel caused by high–temperature Hydrogen attack requires selecting steel with alloying elements such as Cr, Mo and V. The high risks of disbonding of the cladding interface under similar conditions also requires the selection of the most appropriate cladding technology. It is the upmost importance to ensure the interface will support the high–pressure hydrogen and the stresses generated by the heavily loaded internals.

A study around characterizing the DetaClad™ interface was conducted under these extreme operating conditions. More than 150 tests were conducted and coming to the conclusion that DetaClad™ is appropriate for material selection under such demanding operating conditions.

Keywords: DetaClad™, Clad Metal, Corrosion Resistant Alloy, Explosion Welding, Bond Interface, Bond Strength, Disbonding test, hydrogen embrittlement.

1. INTRODUCTION

The Oil & Gas industry has been harshly affected by the ongoing COVID-19 pandemic, and the pre-pandemic trend of turning onto alternative energies has been accelerated these last months. The changing paradigm led the refinery industry to reconsider its processes. Among all the existing processes, the ones using hydrogen at high temperature and high pressure known as Hydrotreating and Hydrocracking are likely the most beneficial as they cover various processes such as conversion of transportation fuels to petrochemical as well as processing of biomass to produce sustainable fuels.

Equipment operating at the conditions mentioned before are usually thick wall pressure vessels lined with stainless steel (clad), typically stabilized AISI 321 or 347. Degradation of dissimilar metal coupled in high temperature, high pressure hydrogen service has been of particular interest in the hydrocarbon refining sector [1-2]. This degradation is related to hydrogen concentration gradients between layers and the formation of phases is very susceptible to cracking. Those conditions can create situations, during temperature transients, where hydrogen builds up at the interface between low alloyed steel and austenitic stainless steel, which can result in disbonding or cracking.

Among the lining technologies, the weld-overlay process (WOL) is very well documented regarding the kinds of damages that lead specifications and codes to preferably select that mode of cladding. But the interface created during explosion welding (EXW) [3] is a metallurgical bond and shows very interesting properties that surpass other cladding technologies in some areas. Although there has been considerable experience employing DetaClad in HTHP applications (particularly in the USA), DetaClad is still suffering from a lack of published data in these environments.

To better understand the behavior of the EXW interface under such environments, a testing program was executed on a thick, low-alloy steel clad plate with stainless steel that would typically be used for such applications. A series of hydrogen disbond coupons were extracted from this clad plate and prepared for testing at an external laboratory. Mechanical properties, microstructure, and the bond strength of this plate were tested in several different conditions to help understand the relationship between processing and properties; particularly, between processing and hydrogen disbond performance. This manuscript summarizes the records of all mechanical test results as well as microstructural evaluations, including hydrogen disbonding tests.

2. MATERIALS AND METHODS

2.1 Procedure

A dedicated stainless steel to carbon steel EXW plate was manufactured following the DetaClad™ process. The plate consisted of a 3.18 mm AISI 321 plate cladder to a 175 mm 542-D-4A backer. The cladder thickness has been selected to simulate the worst case (thinnest) as shown in Figure 1. In a different study [4] the authors confirmed that

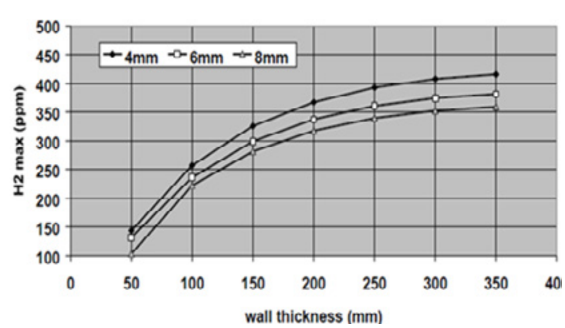


Figure 1: Influence of overlay thickness on hydrogen content at the interface

the stainless-steel acts as a barrier to hydrogen diffusion, and a thicker cladder reduces the hydrogen partial pressure at the interface.

Following cladding, the bonded plate was inspected with automated ultrasonic testing (UT) to ensure an excellent quality bond. Following UT inspections, the 1000 mm x 1000 mm (39” x 39”) plate was cut into four (4) sections as depicted in Figure 2.

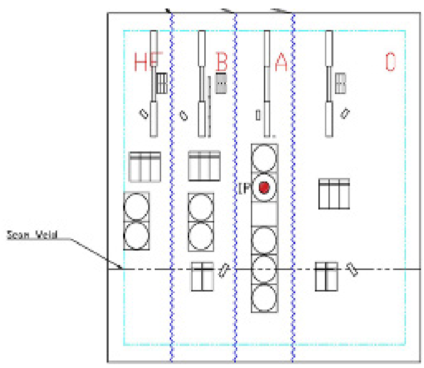


Figure 2: Testing specimen layout incorporating variety of DetaClad™ configurations.

Table 1: Heat Treatment Per Block

BLOCK REF.	SPECIMEN TYPE	HEAT TREATMENT
O	As Cladded	No Heat Treatment
A	Short Post Weld Heat Treatment (SPWHT)	705°C (1300°F) – 480 min
B	Long Post Weld Heat Treatment (LPWHT)	705°C (1300°F) – 1770 min
HF	Head Forming	980 – 1000°C (1796 – 1832°F) holding 180 min
	Normalizing and Quenching	950°C (1740°F) holding 90 min + water quenching
	Tempered	700 – 720°C (1292 - 1832°F) holding 180 min
	Long Post Weld Heat Treatment (LPWHT)	705°C (1300°F) – 1770 min

The Head Forming (HF) section represented the most severe condition by simulating head forming parameters provided by reputed head forming manufacturer Koenig with original quenched and tempered treatment to be applied after hot forming. The short Post Weld Heat treatment (SPWHT) and Long Post Weld Heat Treatment (LPWHT) parameters were shared by the steel mill Dillinger Hütte.

The coupons represent a variety of conditions including DirecAttach™ concept [5]. Developed by NobelClad for the past 15 years simulating the welding of internal components directly onto the cladder, the target was to demonstrate the ability

Table 2: Specimen Details per Sub-Section

BLOCK REF.	SPECIMEN TYPE	LOCATION
O	Shear strength x 3	Interface
O	Shear x 2	Interface + weld
O	Charpy impact x 3	2 mm from interface
O	Tensile strength	½ T
O	Met. Mount x 2	Interface + weld
A	G146 disbond x 3	Interface
A	G146 disbond	Interface + UT defect
A	G146 disbond	Interface + weld
A	Tensile x 2	½ T & ¼ T
B	G146 disbond x 2	Interface
B	Shear x 3	Interface
B	Shear x 2	Interface + weld
B	Charpy x 3	2 mm from interface
B	Tensile	½ T
B	Met. Mount x 2	Interface + weld
HF	G146 disbond x 2	Interface
HF	Shear x 3	Interface
HF	Charpy x 3	2 mm from interface
HF	Met. Mount	Interface
HF	Tensile	½ T

of an EXW interface to support varying level of stresses generated. Avoiding stripping back the cladder prior to welding internals allows for reducing pressure vessel manufacturing costs as well as improving design flexibility.

A total of 8 cylindrical G146 hydrogen disbond coupons [6] were taken from the plate Table 1 as per specimen drawing on Figure 3.

Figure 3: *G146 Specimen Design*

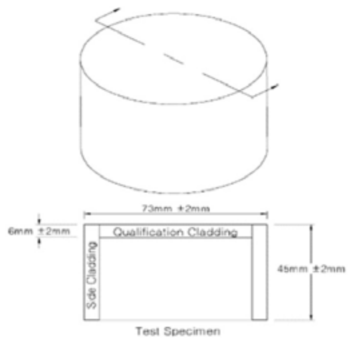


Figure 4: *ASTM G146 Specimen Weld Overlaid on the Edge*

The sides of cylinders were cladded to prevent hydrogen from escaping. To accomplish this cladding, gas metal arc welding (GMAW), was employed to WOL the coupon blanks and put a top seal between the EXW and the sides as shown in Figure 4.

Additionally, a Type AISI 304 attachment was welded to 2 of the ASTM G146 coupons using gas tungsten arc welding (GTAW) root passes and subsequent GMAW passes. The purpose of that configuration was to validate the DirectAttach™ as shown in Figure 5. To learn more about DirectAttach™ click here. The bar was then removed to comply with specimen design Figure 3 before testing.

The disbonding test parameters were determined following the API 934 A recommendation [7]. Considering the thickness range of rolled plates that can be sourced from the market, test conditions from Table 3 and Table 4 Domain B of API 934-A had been selected that leads to Table 3 settings.

Figure 5: *ASTM G146 Specimen for DirectAttach™*

All the tests, including metallography, were conducted in NobelClad's laboratory except the ASTM G146 disbonding test, which was subcontracted to an accredited third-party laboratory named TEC Eurolab.

Table 3: G146 Disbonding Test Conditions

TEMPERATURE °C (°F)	PRESSURE BAR (PSI)	HOLD TIME HR/CYCLE	COOLING RATE °C/H (°F/H)
450 (842)	150 (2175)	48	150 (302)

RESULTS AND DISCUSSION

3.1 Base Materials

Tensile test results at room temperature are summarized in Table 4, including the values reported in the MTR. All the results are within the same range. Charpy results are summarized in Table 5.

Table 4: Tensile Test Results 542-D4A

SPECIMEN LOCATION	SPECIMEN CONDITION	YS MPA (KSI)	UTS MPA (KSI)	EL. %	RA %
½ Thickness	Mill LPWHT	480 (70)	606 (88)	25	76
½ Thickness	As Cladded	597 (87)	711 (103)	26	77
½ Thickness	SPWHT	522 (76)	650 (94)	27	76
Surface	SPWHT	478 (69)	634 (92)	28	77
½ Thickness	Head forming + LPWHT	506 (73)	642 (93)	29	79

Table 5: Charpy Impact Test Results (-29°C)

SPECIMEN LOCATION	SPECIMEN CONDITION	JOULES (AVERAGE)	LBS-FT (AVERAGE)	% DUCTILITY
½ Thickness	Mill LPWHT	205	151	100
Near interface	As Cladded	291	215	100
Near interface	LPWHT	339	280	100
Near interface	Head forming + LPWHT	328	242	100

The mechanical property results confirms that the DetaClad™ process does not alter mechanical properties of the substrate. The Charpy impact tests confirm the assumption of a high ductility zone underneath the interface despite the high energy impact generated by the EXW process.

3.2 EXW Bond Interface

The mechanical properties of a cladded interface are typically evaluated with a shear strength test, and potentially a macro/micro examination. The shear test specimen as shown in Figure 6 and testing method as shown in Figure 7 are compliant with ASME 264 sec. 7.2.1 [9]. Shear test results are presented in Table 6.

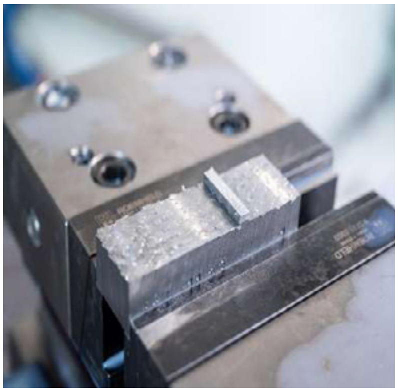


Figure 6: *Shear specimen*

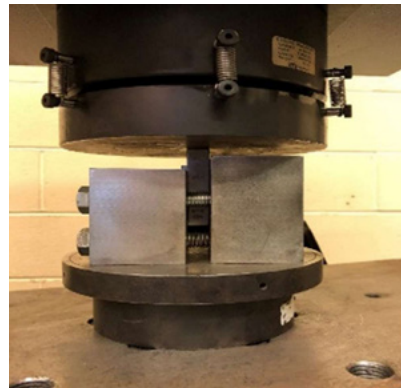


Figure 7: *Shear test according to ASME SA-264*

Table 6: Shear Test Results and Standard Deviation (SD) at Room Temperature

SPECIMEN CONDITION	SHEAR STENGTH MPA (KSI)	SD MPA (KSI)
As Cladded	447 (65)	85 (12)
LPWHT	500 (73)	69 (10)
Head forming + LPWHT	390 (57)	20 (3)

As is typical with shear test results on production plates, the best properties were in the as-clad specimens and the weakest shear results of 390 MPa (57 ksi, average) were from the simulated head forming set. All those results remain 2 to 3 times above 140 MPa (20 ksi) the minimum required by the ASME SA-264 code.

All the fracture surfaces had a generally ductile appearance with no abnormalities as would be expected from shear specimens with very good strength. The typical wavy surface on the micro examination confirmed that failures occurred at the interface and reinforce the reliability of the results (Figure 8 and Figure 9).

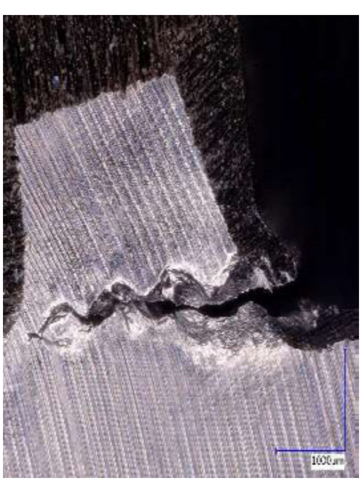


Figure 8: *Optical micrographs of side profile of shear fracture, specimen head forming + LPWHT*

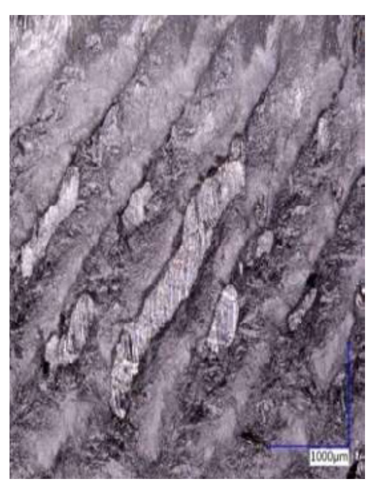


Figure 9: *Optical micrographs of shear specimen fracture surface, specimen head forming + LPWHT*

In the as-cladded condition (Figure 10), the interface showed a clear separation between the Bainite structure of the steel and the austenitic structure of AISI 321 cladder. There was no evidence of martensitic structure potentially detrimental for such applications.

The head forming plus LPWHT specimen (Figure 11) exhibited a layer of ferrite at the interface that can be explained by diffusion/migration of carbon into the stainless-steel matrix during the heat treatment. The lower shear value reported in Table 6 is potentially one consequence of the presence of that ferrite layer. The presence of ferrite was confirmed by the Vickers microhardness measurements presented in Figure 12.

Figure 10: *SEM of metallography of interface - As cladded specimen*

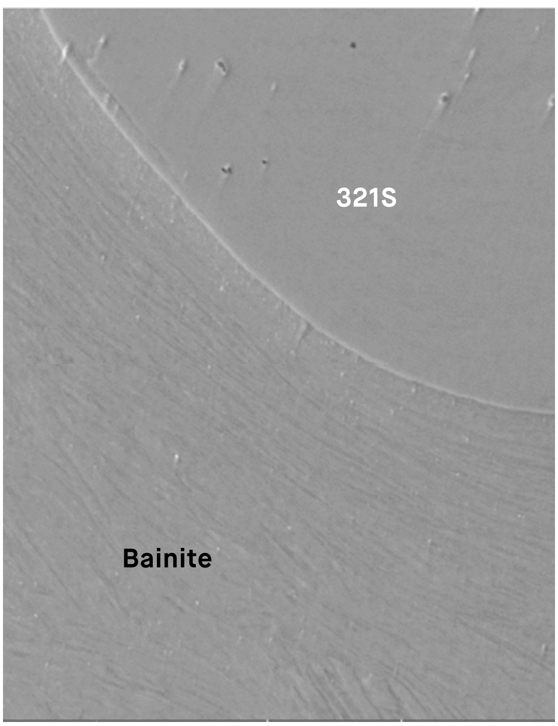
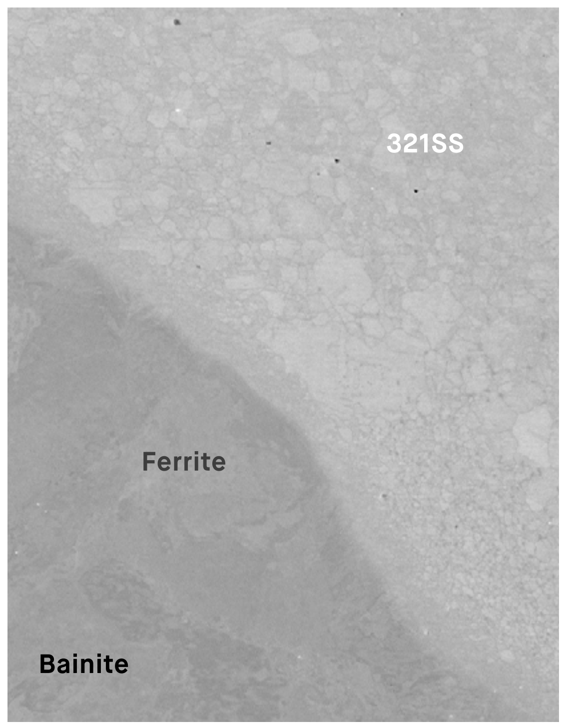


Figure 11: *SEM of metallography of interface - As cladded specimen*



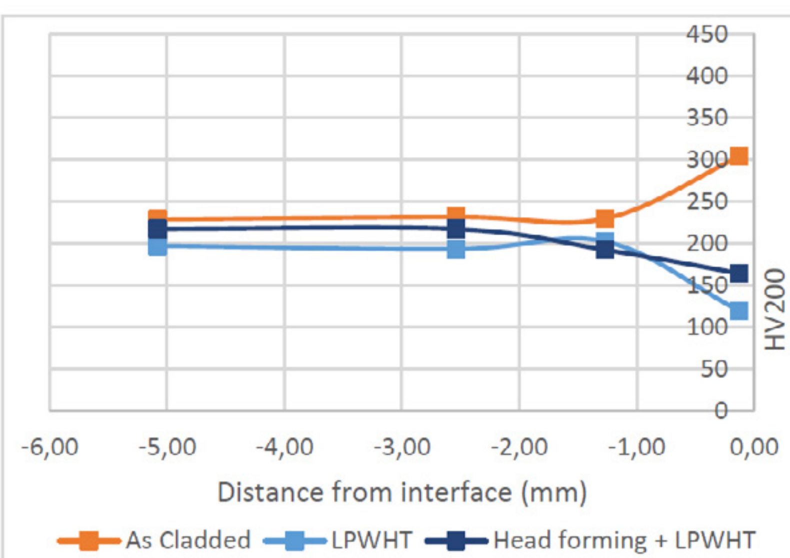


Figure 12: *Microhardness data on steel from EXW interface*

Overall, the as-clad specimens had the highest hardness values. With SPWHT, there was a significant drop in hardness at the interface coinciding with ferrite formation. The simulated head forming, with normalization and quenching, resulted in the most uniform hardness profile with respect to the EXW interface.

Disbonding tests are conducted until the outcomes surpassed the ASTM G146 criteria. A UT examination of the interface enabled identification of any disbonded areas. The UT calibration block was manufactured from the same cladded plate materials and thicknesses to ensure reliability of the findings. However, the flat bottom hole used to calibrate the thresholds during the scan was drilled at a diameter of 3 mm instead 9.4 mm as requested by the code. The effect was an increase in the sensitivity of the disbonding detection.

Results are detailed in Table 7(a) and 7(b) for special configurations.

Table 7(a): ASTM G146 Test Results After 3 Cycles 48 H — Simple Configuration

SPECIMEN CONDITION	FINDING
SPWHT x 2	No indication
LPWHT	No indication
Head forming + LPWHT	No indication

Table 7(b): ASTM G146 Test Results After 3 Cycles 48 H — DirectAttach™ Configuration

SPECIMEN CONDITION	FINDING
DirectAttach – SPWHT	No indication
DirectAttach – LPWHT	No indication

3.3 Cladder

Referring to the prediction methods of the Sigma (σ) phase [8], the ratio factor based on chemical composition of the cladder is equal to 1.7, which is favorable for the appearance of the σ–phase. The σ–phase has a detrimental impact on both the mechanical and corrosion resistance properties of the cladder. Analysis was conducted on 4 specimens that underwent different heat treatments. Results are shown in Figure 13.

Figure 13: *Estimate sigma phase fraction in the AISI 321 cladder near the interface*

The as-cladded specimen did not show evidence of σ–phase as per on Figure 14. However, thermal processing resulted in significant, localized σ–phase near the interface as shown in fig. 15. The σ–phase concentration declines significantly with distance from the interface. It was attenuated by a factor of ~10 between the EXW interface and the surface (Figure 16).

Since there is no delta ferrite in the cladding to start with, σ–phase is slow to form, more difficult than in a weld metal with delta ferrite. The σ–phase at 3 mm from the clad interface is 0.4%, which is tolerable. This indicates a high chemical stability of the clad layer and no observable loss of corrosion resistance.

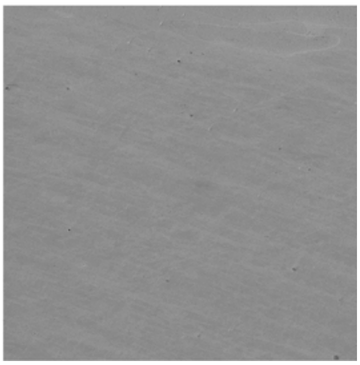


Figure 14: *SEM at 50µM from interface of AISA 321 as cladded specimen*

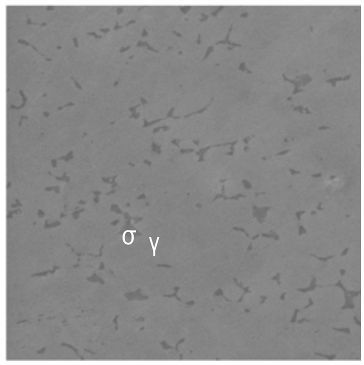


Figure 15: *SEM at 50µM from interface of AISI 321 LPWHT specimen*

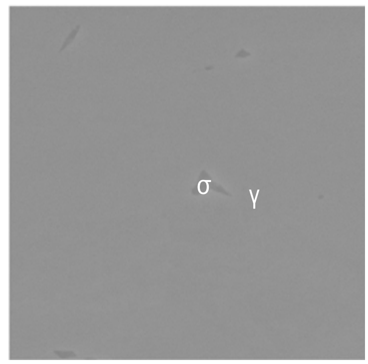


Figure 16: *SEM at 3000µM from interface of AISI 321 cladder LPWHT specimen*

CONCLUSION

The first exhaustive test program conducted on DetaClad™ confirmed the expected outcomes despite the extreme heat treatment conditions and severe ASTM G146 parameters employed. The lack of disbonding of the EXW clad combined with high mechanical properties of the interface provides strong
evidence that DetaClad™ can be integrated into the design of pressure vessels operating in high–pressure, high–temperature hydrogen service. In summary:

- Mechanical properties of the backer material are preserved without evidence of detrimental metallurgical structure like Martensite.
- Cladded interface shows high ductility associated with elevated shear strength widely exceeding code requirement offering an excellent resistance to hydrogen disbonding in refinery high–pressure Hydrogen service.
- EXW does not generate detrimental phases into the cladder such as σ–phase, delaying and limiting its formation during subsequent varying heat treatments.

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