Potential hazards from undetected corrosion in complex equipment: A case study of the destructive separation of an offshore heat exchanger

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This paper describes hazards from undetected corrosion in complex equipment using findings from a collaborative forensic investigation into the destructive separation of a heat exchanger on an offshore gas storage platform. The heat exchanger had been in service for 24 years. The heat exchanger was a conventional shell-and-tube type with both the tubes and shell being manufactured from titanium. However the bonnet and tube sheet were manufactured from carbon steel. The seawater side of the carbon steel tube sheet had been protected from corrosion by titanium cladding.

The investigation revealed localised corrosion of the carbon steel tube sheet in areas exposed to acidic condensate containing hydrogen sulphide. Corrosion was galvanic in nature and had occurred where, by design; the carbon steel–titanium interface was exposed. The results showed that hydrogen, generated cathodically by the galvanic corrosion, had formed titanium hydride in the interfacial region of the titanium cladding.

The evidence indicated that the separation of the tube bundle and shell from the bonnet was probably initiated when a large area of the cladding bond interface failed suddenly due to hydride formation. The final destructive separation of the tube bundle can be explained by the deformation of the cladding after complete failure of the bonded interface with the tube sheet.

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1. Introduction

1.1. Background

A horizontal shell-and-tube heat exchanger failed on an offshore storage platform. The tube bundle and shell separated completely from the bonnet with considerable force and approximately 10 tonnes of hydrocarbon gas was released [1].

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Adjacent equipment on the platform was damaged by the force generated from the separation of the heat exchanger. There was further extensive damage in the fire and explosion that ensued when the gas cloud ignited. Personnel on the platform were evacuated successfully and there were only minor injuries.

The Health and Safety Laboratory (HSL) carried out a forensic metallurgical investigation for the Health and Safety Executive (HSE) to determine how the heat exchanger had failed. This investigation was overseen by a collaboration of technical experts from HSL, HSE and the platform operator with industrial experts from two independent organisations. The Offshore Division of the HSE issued a Safety Alert [2] to make the results of the investigation available to other users.

The original function of the heat exchanger was to cool hydrocarbon gas from wells before pumping on-shore. In recent years, however, the heat exchanger had been used on a cyclic basis, cooling gas being pumped off shore into the formations for storage during summer months and cooling gas extracted from the formations during winter months. It was reported that gas pumped for storage was pre-dried before passing through the heat exchanger but gas extracted from the formations contained moisture that was intended to condense in the heat exchanger.

1.2. Design aspects

The heat exchanger was a conventional shell-and-tube bundle design that was manufactured in 1983 for a gas pressure of 100 bar (1450 psig) in the tubes and a shell seawater pressure of 10.3 bar (150 psig). At the time of failure, the gas pressure was 90 bar (1300 psig) and the cooling water pressure was 10 bar (145 psig). The heat exchanger was approximately 9 m long overall with a shell diameter of 1 m and a bundle of 1130 tubes, each 6.5 m long. The tube specification was \( \frac{3}{4} \) in. OD, 16 BWG tubing to ASTM/ASME SM338 Grade 3 titanium. Fig. 1 shows the main components schematically.

The tube bundle and shell were manufactured from titanium. The bonnet and tube sheet were manufactured from carbon steel (CS) but the seawater side of the tube sheet had been clad with 13 mm thick titanium. The cladding had been applied by explosive bonding and every tube-to-cladding joint was circumferentially welded into a recess in the titanium cladding sheet, Fig. 2.

The heat exchanger was designed to use titanium for seawater contact and a combination of titanium and carbon steel for surfaces in contact with the hydrocarbon gas and condensate. The interface between the titanium and carbon steel surfaces on the gas side was inside the holes of the tube sheet. A significant design feature, therefore, was the exposure of the titanium–carbon steel interface to the high pressure gas stream and condensate.

Tube–tube sheet joints are a critical feature of heat exchanger design. A number of joint designs can be used which range from welded joints to tubes that are mechanically expanded into sealing grooves. In the heat exchanger that failed, the tube to cladding sheet joint was an automatic tungsten inert gas (TIG) weld made from inside each tube. The weld was effectively 0.8 mm thick compared with the 1.65 mm wall thickness for the tube so the load bearing area of the weld was less than that of the tubing. Thus any load or strain transmitted from a tube to the tube sheet would have caused the highest stress levels to occur in the weld metal. A further important feature was that the welds connected each tube to the cladding sheet. Consequently the explosively bonded interface was part of the load path and any load or strain passing between the tube bundle and the steel tube sheet was transmitted across the interface.

The heat exchanger was fitted with sensitive hydrocarbon detection on the water-side to indicate leakage of gas through to the water side. There was also a water-side bursting disc which was estimated by the operator to be capable of withstanding the simultaneous failure of at least two tubes.

![Fig. 1. A diagram showing the key features of the heat exchanger and the seawater and gas flows in normal operation.](image-url)
1.3. Failed components

A number of critical components in the heat exchanger structure had failed, as identified in Fig. 3, and were recovered from the platform after the incident. The failed components of particular interest were:

- The cladding and the tube sheet to which it had been bonded, Figs. 4 and 5.
- The 1130 fractured welds between the tube and the cladding, Fig. 6.
- The fractured girth flange from the shell.
- One fractured tube.
- The failed seawater side bursting disc.

The components were examined metallurgically and fractographically at HSL, Buxton, to characterise individual fracture modes and their respective contributions to the overall failure of the heat exchanger.
2. Examination of the failed components

2.1. The cladding

2.1.1. Fractography

The fracture surfaces produced by the separation of the cladding from the tube sheet had regular undulations that were spaced approximately 1.7 mm apart, Fig. 7. The undulations formed approximate concentric curves that had ripples along
their length. The curvature of the waves decreased from the lower part of the cladding towards the top and they appeared to radiate from a central point near the bottom of the cladding. Matching fracture features were found on the titanium cladding and the carbon steel tube sheet. The undulations and curvature were characteristic of features that would be expected for a fracture path that followed the interface produced by explosively bonding titanium to carbon steel [3]. The uniformity of the features on the fracture surface indicated that the explosive cladding process had produced a consistent bond across the whole interface between the titanium cladding and the carbon steel tube sheet.
Areas of orange/brown\(^1\) coloured corrosion products were present on the titanium cladding fracture surfaces, particularly the areas closest to the incoming gases. Dark grey areas were visible around circumference of the tube holes in the lower half of the cladding, Fig. 8. Furthermore, in the lower half of the cladding, a network of short, intersecting cracks (mostly

\(^1\) For interpretation of colour in Figs. 8 and 16, the reader is referred to the web version of this article.
perpendicular to the cladding interface) was present in the material surrounding the tube holes and small fragments had been lost at some positions from the edge of a hole, Fig. 9. Larger cracks were visible in some places further from the holes. The short intersecting cracks were most frequently found in the areas with a darker grey colouration.

Sample areas were removed from the upper section and lower section of the cladding for examination in the scanning electron microscope. This examination indicated that the wavy pattern of the surface was caused by separation along the distorted interface where the cladding had been bonded to the steel tube sheet, Fig. 10. There were no characteristics of conventional failure modes, such as ductile micro-void coalescence, cleavage fracture, or the formation of striations from progressive fracture, Fig. 11. Fine ridges were present in a few areas at the highest and lowest parts of the waves. The ridges suggested that only a limited amount of ductility had occurred when the titanium cladding separated from the steel tube sheet.

2.1.2. Metallography

Microsections were prepared from the cladding at a number of positions from the upper and lower sections. The microsections were mounted and prepared to provide through-thickness samples that intersected the surface that had been explosively bonded to the carbon steel tube sheet. The microsections were prepared metallographically and etched in Kroll’s reagent for examination under an optical microscope.

Microscopic examination revealed that the cladding had an alpha phase microstructure consistent with commercially pure titanium, Fig. 12. The material had a relatively uniform equiaxed grain size across the thickness of the sheet but there was some alteration to the grain size and shape at the tube-cladding welds and adjacent to the explosively bonded interface. The heat-affected zone of the welds and the cladding had recrystallised and the grain size was increased. The weld metal itself had a coarse grained columnar structure that contained acicular alpha phase. There was a deformed zone adjacent to the bond interface, which contained very fine alpha grains. The deformed zone showed some evidence of recrystallisation, which indicated that the cladding had been heat-treated after the explosive bonding operation.

While the bulk microstructure of the cladding consisted of equiaxed alpha phase, there was a thin surface layer which appeared to contain a second (dark etching) constituent with an acicular (i.e. needle-like) morphology. The equiaxed structure and the acicular constituent are indicated in Fig. 13. The microstructure varied from individual needles in the alpha phase matrix to a continuous layer at the bond interface that was composed entirely of the acicular phase, Fig. 14. Where present as a continuous layer, the layer was estimated to range from 20 μm to 100 μm in thickness. The characteristics of the acicular layer were:

- It was thickest at the edges of tube holes, i.e. the point where the interface between the titanium cladding and carbon steel tube sheet had been exposed to the gas stream.
- It was thicker at the edge of tube holes in the lower section of the heat exchanger than at the edge of tube holes in the upper section.
- Scattered needles of the acicular phase were present up to the edge of the cladding.
- Microscopic cracks were associated with the acicular constituent; the crack orientations ranged from parallel to perpendicular with respect to the bond interface. Most cracks were at the edges of holes in the lower part of the heat exchanger, i.e. where the acicular layer was thickest. The cracking appeared to correspond to the cracks and detached fragments visible on the bonded surface of the cladding.

Metallographically, the appearance of the acicular constituent indicated that it was likely to be an inter-metallic compound such as titanium hydride, titanium oxide or titanium nitride.
2.1.3. Chemical analysis

Chemical analysis was carried out on samples of the cladding to identify the composition of the acicular constituent in the microstructure at the bond interface. The analysis was carried out by two different techniques; one being a bulk analysis technique and the other being a microscopic method. The bulk analysis technique involved removing small fragments weighing approximately 500 mg. This involved sawing to release samples that were approximately 10 mm long with a cross section of 3 mm × 3 mm. Pairs of samples were taken; the first of which included part of the bond interface, and the second immediately below it, i.e. approximately 4–5 mm from the bond interface. Four pairs of samples were prepared, two pairs from the upper section of the cladding sheet, and two pairs from the lower section. Hydrogen contents were determined by Thermal Conductivity Fusion. The results of the analysis are summarised in Table 1.

The original test certificate for the titanium cladding gave a hydrogen content of <0.01% (<100 ppm) at the time of manufacture. Based on the values obtained in this investigation from material approximately 4 mm from the bond interface, the actual hydrogen content of the cladding was probably between 20 ppm and 30 ppm. It can also be seen that the hydrogen...
content was approximately 10 times higher at the bond interface in the upper part of the heat exchanger. However, the highest hydrogen levels were recorded at the bond interface in the lower part where the results showed hydrogen levels 15 times to 30 times higher than the material 4 mm from the bond interface.

Microscopic chemical analysis was carried out on prepared microsections by Secondary Ion Mass Spectrometry (SIMS). This method can obtain composition data from very small areas and thus provide details of concentration variations in structures that are not homogenous. SIMS results confirmed that there was significant hydrogen enrichment in material at the bond interface to a depth of between 60 μm and 150 μm. The results did not reveal any constituents other than titanium and hydrogen.

2.2. The tube sheet

2.2.1. Visual examination

Visual examination of the bond surface of the tube sheet, Fig. 15, showed that corrosion had taken place over the whole of the surface. The corrosion product layer was orange/brown in colour and was generally thin, consistent with it having been formed following the separation of the cladding from the tube sheet. On the lower half of the tube sheet, which would have been at a cooler temperature than the upper half when the heat exchanger was in operation, it was apparent that significant corrosion had occurred in areas where the clad surface met the tube holes, Fig. 16. The corrosion appeared to be most severe towards the lowest part of the holes, consistent with corrosion caused by the presence of liquid water in the tubes. The corrosion had formed rounded cavities due to localised loss of metal at the edge of the hole in the carbon steel. Measurements with a digital vernier gauge indicated that the corroded cavities ranged from 0.9 mm to 3.4 mm in depth. The surfaces of the cavities had a thin layer of corrosion products that appeared to be of similar thickness to the layer of corrosion products over the bond surface.

2.2.2. Metallography

It was difficult to extract metallographic sections from the tube sheet because of the extensive machining required due to its thickness and diameter. Small scoop shaped samples were therefore machined from the tube sheet using a rotating cutter in a patented cutting jig. The samples were cut offset from the centre line of a tube so that the complete circumference of one hole and part of an adjacent hole were included.

Microsections were prepared from the scoop samples and metallographic examination after etching in nital reagent showed that the tube sheet had a fine-grained microstructure consisting of ferrite and pearlite. The microstructure of the tube sheet was characteristic of hot rolled or forged carbon steel, consistent with ASTM A350-87a LF2 as specified by the manufacturing drawings for the heat exchanger. Microscopic examination also confirmed that the cavities at the edge of the lower tube holes had been formed by severe localised corrosion. Localised corrosion was not evident at the edges of the upper tube holes. Light, uniform corrosion was also visible on the surfaces along the bore of tube holes from the upper section of the heat exchanger. A relatively thin layer of black corrosion products was evident on all the corroded surfaces.

2.2.3. Energy dispersive X-ray analysis

The corrosion product layer, position indicated in Fig. 16, was subjected to Energy Dispersive X-ray Analysis using a scanning electron microscope. The results of the analysis showed that the principal constituents of the layer were iron, sulphur and oxygen. This suggests that the scale was iron sulphate or iron sulphite. In moist air, the water vapour and oxygen present will convert iron sulphide to iron sulphite and/or iron sulphate. Given that the gas-side of the heat exchanger would have
had an extremely low oxygen content, the results indicate that corrosion had formed a layer of iron sulphide on the inside of the holes in the tube sheet.

Natural gas from an underground reservoir is likely to contain carbon dioxide, hydrogen sulphide and water in varying proportions. As the hydrocarbon stream cooled in the heat exchanger, it is likely that the condensate would have been acidic due to the dissolved carbon dioxide and/or hydrogen sulphide. The fact that sulphur was one of the principal constituents in the corrosion product layer indicates that the main acidic component of the condensate was likely to have been hydrogen sulphide.

2.3. Fractured tube to cladding welds

2.3.1. Visual examination and fractography

The 1130 tube to cladding welds had all failed. It was also evident that one tube had failed inside the tube bundle in addition to having failed at the cladding sheet weld. The weld fracture surfaces were examined visually and samples were removed for more detailed fractographic examination with a stereo-optical microscope. The tie bar welds and the bundle runner welds were also examined. The tube to cladding welds, the tie bar welds and the bundle runner welds had all failed in a ductile fracture mode as a result of mechanical overloading. The tube to cladding welds contained levels of fine, uniformly scattered gas pores. It was estimated visually that the total volume fraction of the porosity varied from 1% to 15%, but up to 30% was observed occasionally. While the porosity would have reduced the strength of the tube to cladding welds, there was no evidence that the ductile failure mode had been affected.

More detailed examination of the areas of ductile failure revealed two different types of appearance:

(a) Flat areas approximately perpendicular to the tube axis and coincident with the end of tube and the weld root centre-line. There was evidence of significant welding porosity in these areas. The fracture appearance in the flat areas was relatively featureless. This was the predominant type of fracture appearance of the tube to cladding sheet welds.

(b) Slanted areas with a slightly fibrous appearance were also visible. These areas occurred a short distance from the welds and followed planes that were clearly within the parent metal of the tube material. There was no evidence of any material deficiencies within the tube material.

In general, the majority of the fractures had a large single area (representing from 60% to 90% of the cross-section) with the type (a) fracture appearance, and the remaining area was the type (b) fracture. A significant number of the fractures consisted entirely of the type (a) appearance while only a small number of fractures had a completely type (b) appearance.

A higher magnification examination of the fracture surfaces was carried out using the scanning electron microscope. This examination showed that the fracture mode in type (a) and type (b) areas both consisted of ductile failure by micro-void coalescence, Fig. 17. Very small regions of cleavage fracture were observed in the type (a) areas where weld metal had fractured in a brittle manner. There was no evidence of progressive crack growth by a fatigue mechanism in the type (a) or type (b) areas. It was clear, therefore, that the only difference between the type (a) and type (b) fractures was the position of the failure with respect to the original weld. In other words, the dominant failure mode, producing the type (a) appearance, was ductile failure of the weld metal, while the secondary mode, which produced the type (b) appearance, was also ductile failure but of the tube material.

It was not possible to identify a consistent pattern in the distribution of the fractures that displayed either type (a), or type (b), or a combination of both types. However, on individual fracture surfaces where both types were present, there was a strong tendency for them to occur symmetrically on opposite side of the tube axis. This indicates that the loading
responsible for failure of the tube to cladding welds probably involved bending which produced type (a) fracture where ductile failure initiated at the weld root and type (b) where fracture occurred in the tube material.

2.3.2. Metallographic examination

Samples were removed for microsections from a sample of the welds. The sections were prepared metallographically and etched in Kroll’s reagent for microscopic examination. Microscopic examination revealed that the tubes had a fine-grained, alpha phase microstructure characteristic of commercial purity titanium in the wrought condition. A range of microstructures were observed in the weld ranging from coarse, equiaxed grains where the tube or cladding sheet been recrystallised by the heat of welding, to large columnar grains with acicular alpha phase where weld metal had solidified. Gas porosity was evident in the weld metal but there was no evidence of any adverse constituents, such as hydride or oxide phases, from welding.

Microscopic evidence indicated that the welds were of the specified size. It was also evident that the gas side and seawater side surfaces were smooth and that there had been no degradation in service by corrosion, erosion or by the diffusion of hydrogen. No secondary cracks were visible in the weld sections as might have been expected if the welds had failed by progressive cracking, for example by fatigue.

2.4. Fractured welds between the tube and cladding

There were additional welds where the bundle tie rods and rails were joined to the cladding. These welds had also failed and the appearance of their fracture surfaces was characteristic of ductile failure accompanied by significant plastic deformation.

2.5. Fractured shell girth flange

According to the manufacturing drawings, the girth flange had been joined to the shell by two circumferential welds, Fig. 18. It was clear that the girth flange had fractured almost entirely through the shell material just beyond one of the two welds. There was extensive plastic deformation of the fractured section such that it had become an irregular, twisted shape with little resemblance to the original circular shape of the tube bundle shell. The original perpendicular relationship between the flange surface and the shell was recognisable although the angle had become increased to significantly greater than 90°. The increase in the angle between the flange and tube bundle shell indicated that the flange had been deformed towards the chamber of the heat exchanger. Subsequent examination revealed localised, through-thickness bending of the tube bundle shell around the full circumference of the heat exchanger. The direction of bending was inwards, as explained in Fig. 18. The direction of localised bending of the shell was, therefore, consistent with the direction in which the girth flange had become deformed.

![General arrangement before failure](image)

**Fig. 18.** Original arrangement of girth flange and position of final failure caused by pressurisation and deformation of the separated cladding.
Examination of the fracture surfaces indicated that the failure of the shell material was characteristic of ductile fracture due to bending overload. There were no indications on the fracture surface of pre-existing material defects in the tube bundle shell, the flange or the welds. The fracture appearance did not have any characteristics of progressive failure.

A macrosection was prepared from the fractured part of the girth flange. Examination of the etched section revealed no evidence of any material or manufacturing deficiencies in the shell and flange parent materials. Similarly, there were no indications of imperfections in the welds between the tube bundle shell and the flange.

2.6. Tube failure within the bundle

It was apparent that one tube had failed inside the bundle (in addition to its failure at the cladding sheet weld) because directly after the incident, it was found protruding by a length of approximately 1.4 m from the fractured ends of all other tubes. All other tubes were only slightly displaced (20–100 mm) from their original positions and the displacement was in the opposite direction. The position of the tube failure in the bundle was located by passing a length of welding wire down the tube as a probe. This positioned the failure approximately 2 m from the rear of the tube bundle. Once located, the failure was exposed by removing short lengths of tubes between the baffle plates that were nearest to and overlying the indicated position.

The fracture was found to have occurred close to the end of the bundle at the transition between the bend and the straight section of the upper part of the tube. In fact, the two fractured ends had separated by approximately 1.5 m, i.e. the same distance as the length of tube protruding from the bundle after the failure. The fracture on the front section of the failed tube was cut out with approximately 200 mm of the tube attached. The fractured end was examined using a stereo-optical microscope and the failure was found to be typical of a ductile failure caused by tensile overloading.

2.7. Examination of the seawater side bursting disc

The bursting disc had a star shaped fracture pattern with six petal shaped sections which remained attached to the circumference. It was apparent that the star shaped pattern was caused by the pre-scored grooves in the disc. The petals from the failed disc were bent in two directions. The most severe bending was consistent with flow outwards from the seawater side of the heat exchanger, i.e. the intended direction of failure. The least severe bend was near the tips of the petals and was consistent with a reversal of flow after the disc had failed. The fracture surfaces appeared to be smooth and featureless, characteristic of a ductile shear failure that occurred when the membrane stress at the base of the pre-scored grooves in the bursting disc exceeded the strength of the material. This fracture mode was therefore consistent with an event on the seawater side during which the water pressure exceeded the design pressure of the bursting disc.

2.8. Other observations

There was no evidence of fretting or wear of tubes due to rubbing at the points where they passed through baffle plates. Similarly, holes in the baffles had not been enlarged by wear. The outer surfaces of the tubes were generally clean although accumulations of sand and marine debris were present at some points, particularly the far end of the tube bundle. There was no significant erosion damage of the deflector plate position over the seawater inlet.

3. Assessment of the failure mode

3.1. Materials and manufacture

The results of this investigation have indicated that components examined from the heat exchanger had been manufactured according to the specifications given for parent materials in the manufacturer's drawings. The failure of the heat exchanger involved failure of:

i. The explosive bond between the titanium cladding sheet and the carbon steel tube sheet.
ii. All welds between the cladding sheet and the tube bundle.
iii. The shell of the tube bundle adjacent to the girth flange.

Explosive bonding produces a disturbed interface where the metals being bonded undergo a wave like deformation [3]. It is likely that the process of cladding the tube sheet with titanium was carried out to ASTM B898 [4]. The interface failed completely during the incident so it was not possible to test the quality of the bond that had been achieved at the time of manufacture against the requirements of ASTM B898. However, fracture surfaces on the cladding sheet and the tube sheet both showed evidence of a pronounced wave pattern across the whole area which indicated that a bond had existed before the failure. The wave pattern was consistent with a satisfactory explosive bond having been produced at the time of manufacture. The microstructure of the titanium and carbon steel indicated that the cladding sheet and tube sheet had both been deformed in the way that would be expected for explosive bonding. The cladding sheet and tube sheet had also been subject
to a stress relief heat treatment after explosive bonding. There was no evidence from this investigation to suggest, therefore, that the explosive bond had failed due to a manufacturing deficiency.

The tube to cladding sheet welds, the tie bar welds and the bundle runner welds had all failed in a ductile fracture mode as a result of mechanical overloading. The tube to cladding sheet welds contained pores that had reduced their cross section by 1–15%, but by up to 30% in a few instances. While the porosity would have reduced the weld strength, there was no evidence that the ductile failure mode of the tube to cladding welds had been affected by the level of porosity.

The failure of the tube bundle shell had occurred through the shell parent material at the edge of the welds with the girth flange. There was no evidence to indicate that the welds between the shell and the girth flange had weakened the shell material.

In conclusion, no evidence was found in this investigation to suggest that material and/or manufacture deficiencies had contributed to the failure of the heat exchanger.

3.2. Design features

The heat exchanger was designed to use titanium for surfaces in contact with seawater and a combination of titanium and carbon steel for surfaces in contact with the hydrocarbon gas. The transition between the titanium and carbon steel surfaces on the gas side occurred inside the holes of the tube sheet. By design, the titanium–carbon steel transition on the gas side was the interface produced by explosive bonding the cladding sheet to the tube sheet. It was a significant feature of the failed heat exchanger that the titanium–carbon steel interface was exposed to the high pressure gas side.

The tube–tube sheet joints are a critical feature in heat exchanger design. A number of joint designs can be used which range from welded joints to tubes that are mechanically expanded into sealing grooves. In the heat exchanger under investigation, the tube to cladding sheet joint was a TIG (tungsten inert gas) fusion weld made by an automatic process from inside each tube. The weld was effectively a single sided butt weld with a minimum throat dimension of approximately 0.8 mm compared with the 1.65 mm wall thickness for the tube. In fact the quality assurance records show that the manufacturer’s acceptance criteria for these welds were a minimum throat width of 0.98 mm and a minimum push out force of 4 tonnes. It can be seen that with this design, the load bearing area of the weld that was less than that of the tubing. Thus any load or strain transmitted from a tube to the tube sheet would have caused the highest stress levels to occur in the weld metal. A second important feature of weld design was that the welds connected tubes to the cladding sheet but not directly to the steel tube sheet. Consequently the explosively bonded interface was part of the load path and load or strain passing between the tube bundle and the steel tube sheet would have to be transmitted across the interface.

3.3. Condition of the heat exchanger prior to failure

The evidence suggests that at the time of the failure, there had been no significant corrosion of the titanium parts of the heat exchanger whether they had been in contact with seawater or the hydrocarbon gas stream. There was also no evidence of degradation by erosion or fatigue, of the tubes, baffle plates or the tube to cladding sheet welds. No features indicative of fatigue or stress corrosion cracking were observed, which would have indicated that these processes could have been involved in the failure of the tube shell at the girth flange.

There was significant localised deterioration of the carbon steel tube sheet due to galvanic corrosion. Locally corrosion had caused several millimetres of metal loss at the interface of tube holes in the lower section of the heat exchanger. Based on the presence of sulphur in the corrosion products, and the position of the metal loss, it is clear that corrosion of the carbon steel was caused by contact of the two dissimilar metals in wet conditions and in the presence of hydrogen sulphide.

Microscopic examination revealed clear evidence of significant degradation in the mechanical properties of the explosive bond between the titanium cladding sheet and the carbon steel tube sheet. The degradation was caused by galvanic corrosion and by extensive formation of titanium hydride in the cladding sheet along the bond interface. A layer of titanium hydride, which was mainly intermittent but continuous at the edges of tube holes, had been formed over a large proportion of the bond interface in the lower part of the heat exchanger. There was a generally thinner and intermittent hydride layer in the upper area. Cracking was associated with the titanium hydride where it was present as a continuous layer at the edges of upper tube holes.

It was not possible to quantify the degradation in the mechanical properties of the bond interface because the complete area had failed. However, typical Charpy impact test results provided by DMC Inc., indicate that a very low fracture toughness can be expected in explosively bonded materials when the fracture plane coincides with the bond interface. The presence of titanium hydride would have adversely affected the fracture toughness of the bond interface in three ways. Firstly, the formation of titanium hydride is accompanied by an 18% volume expansion that would cause a jacking or wedging stress across the bond interface [4]. It is possible that the cracking observed where the microstructure contained the highest level of titanium hydride could have been caused by this jacking or wedging effect. Secondly, it is known from the literature that tensile tests conducted on titanium alloys containing hydrides failed with zero strain to failure [5]. Therefore, it is probable that the interface would have had little mechanical strength in areas that contained significant quantities of titanium hydride. A third mechanism is also possible if, as is known to occur in steels, hydrogen becomes trapped and causes pressurisation of microscopic voids and interfaces.
The absence of the titanium hydride at any other position in the titanium tubes, and the coincidence of the localised corrosion of the tube sheet with the formation of titanium hydride at the bond interface are significant observations. The observations show that the localised corrosion and the presence of the titanium hydride were obviously related. This can be explained by the liberation of hydrogen as the cathodic step in the corrosion reaction. In aerated conditions, the cathodic reaction in aqueous media would normally be the reduction of oxygen. However, the hydrocarbon gas stream would be essentially free of oxygen and it is reasonable to expect, therefore, that the cathodic reaction produced hydrogen. It is concluded that the degradation in mechanical properties of the explosive bond through hydride formation would have occurred progressively. Thus the progressive degradation of the bond with the titanium cladding was directly attributable to galvanic corrosion of the carbon steel tube sheet.

3.4. Mechanisms of component failure

Two types of failure mechanism can be identified for components that had failed in the heat exchanger. The first failure mechanism involved separation of the titanium cladding sheet. For the reasons given in Section 3.3, the titanium–carbon steel interface produced by the explosive bonding would have had inherently low fracture toughness as manufactured. The evidence shows that the fracture toughness of the bond would have been further reduced with time as the layer of titanium hydride spread out from the tube holes. It is considered, therefore, that the bond interface failed when the titanium hydride layer had spread further than a critical distance from the tube holes; in fracture mechanics terms, the area of titanium hydride had exceeded the critical defect size for fast fracture. It is also possible that the applied stress acting across the bond interface at the time of failure could have been increased due to:

- Jacking and/or wedging due to the increased volume of titanium hydride.
- Pressurisation on the plane of the interface due to the internal area of the cavities produced by localised corrosion.
- Tensile and/or bending stresses imposed by deflection of the tubes.
- Thermal stresses from the difference in thermal expansion coefficients between titanium and carbon steel.
- Blocking of tubes by methane hydrate.

However, it is not possible to determine the relative contributions that each of these made to the failure, or whether there was more than one source of stress on the bond interface at the time of the incident.

The second failure mechanism, which affected the largest group of components, was mechanical overloading. Components in this group showed no evidence of degradation in service. The components that had failed by mechanical overloading included:

i. The bursting disc had failed in the manner that would be expected for over-pressurisation of the seawater side.
ii. The tube bundle shell had failed adjacent to the girth flange due to mechanical overloading by localised, through-thickness bending of the shell material. The failure was consistent with leverage of the flange by the deformation of the cladding sheet.
iii. All tube to cladding sheet welds had failed. The welds had failed by an overload mechanism that involved bending resulting from the dome shaped deformation of the cladding sheet and/or buckling of the tubes.
iv. One tube had failed within the bundle by a tensile overload mechanism.

3.5. Probable failure sequence

Three key stages can be identified in the failure of the heat exchanger as explained in Figs. 18–20. The evidence suggests that the primary stage in the failure was galvanic corrosion of the carbon steel tube sheet at the interface with the titanium cladding. Fig. 19. Corrosion occurred in the wet conditions existing in the lower tubes. The presence of the sulphur in the corrosion product demonstrates that the condensate was acidic because it contained dissolved hydrogen sulphide from the gas stream. This is not to say that the gas stream was sour, i.e. containing ~1% hydrogen sulphide, but it does indicate that the relative proportions of water and hydrogen sulphide were such that the condensate was acidic.

There are two reasons why the presence of hydrogen sulphide is important to the failure. As discussed by Kane [6], it is generally considered that the rate of corrosion of carbon steel increases because hydrogen sulphide is source of hydrogen ions when dissolved in water. Secondly, hydrogen sulphide promotes the absorption of atomic or nascent hydrogen. Due to the presence of hydrogen sulphide in the gas stream, corrosion of the carbon steel generated hydrogen that diffused along the interface between the titanium cladding and the tube sheet. The hydrogen formed a layer of titanium hydride in the cladding which had spread outwards from the tube holes degrading the fracture toughness over an increasing proportion of the bonded interface. It is not possible to quantify the time that the initial stage would have taken but it is considered probable that it would have required a significant part of the service life of the heat exchanger at the time it failed.

The results of the investigation indicate that the second stage, Fig. 20, was disbonding of the cladding sheet. This probably occurred in steps as disbonded areas around each tube increased in size until they linked up. The final stage in the failure probably began when the combined disbonded area exceeded a critical size and the remaining interface disbonded suddenly. The detached cladding sheet would then have been deformed rapidly into a domed shape. The rapid deformation of the cladding...
sheet would have simultaneously caused a large number of tube to cladding sheet welds to fail suddenly and produced a severe leverage effect on the girth flange, Fig. 18. It appears likely that this caused a rapid escape of hydrocarbon gas into the seawater side that in turn caused the bursting disc to fail. Even though the bursting disc failed, it would appear that there was sufficient pressurisation of the bundle shell to cause final failure of the deformed area next to the girth flange. In other words, the tube shell became pressurised at a rate that could not be relieved by the failure of the bursting disc. The steps in the final stage of failure and the resulting separation of the tube bundle and shell are likely to have occurred almost instantaneously.

3.6. Survey of literature on hydriding of titanium

3.6.1. Effect of titanium hydride on mechanical properties

The hydrogen content of titanium is controlled closely during manufacture. Once manufactured, titanium and titanium alloys can absorb hydrogen from the environment under certain conditions, particularly at above ambient temperatures such
as might occur during heat treatment or welding. A maximum hydrogen content of 150 ppm is normally applied to commercial purity titanium but in most cases the actual hydrogen content is likely to range from 20 ppm to 50 ppm. Berger [7] showed that the room temperature impact strength of titanium was reduced by 8 times when the hydrogen content increased from 20 ppm to 230 ppm. The other mechanical properties, yield strength, tensile strength and elongation, were not affected by increases in hydrogen content up to 230 ppm. It is interesting to note that Philips [8] observed that the absorption of large amounts of hydrogen (actual levels were not given but they were probably >230 ppm) in laboratory tests resulted in cracking and spalling of the hydride layer. This was probably caused by the fact, as recognised by Alvarez and others [4,5] that the volume of titanium hydride is 18% greater than alpha titanium and so its formation would generate large stresses.

3.6.2. Titanium hydride formation

The published work on hydride formation in commercial purity titanium and embrittlement has been concerned with thin-walled tubing as used widely in heat exchangers [9]. The main purpose of the studies appears to have been one of avoiding brittle failure of titanium tubing in power plant condensers. The consensus of the work [9–11] was that hydride embrittlement of titanium tubing involves three factors:

i. A corrosion mechanism for producing nascent hydrogen.

ii. A solution pH less than 3 or greater than 12, or impressed potentials more negative than −0.7 V (versus SCE).

iii. A temperature >80 °C that will allow a significant rate of hydrogen diffusion through the tube wall thickness.

The current view is that embrittlement of titanium tubes can be avoided by removing one or more of these three factors. It is important to distinguish between the formation of titanium hydride, by chemical/electrochemical processes, and the embrittlement that it may cause through the wall of condenser tubing by the physical process of hydrogen diffusion. It is self evident that titanium hydride will not be produced unless hydrogen is generated and consequently hydride formation is controlled by factor (i) and factor (ii). However, if titanium hydride is formed, the extent of embrittlement through the wall of tubing will be slight unless the temperature is >80 °C because the hydride will remain as thin surface layer. A thin (~100 µm thick) surface layer of brittle titanium hydride is unlikely to cause brittle fracture where the wall thickness of tubing is greater than 1 mm. In other words, the thickness of the hydride layer is determined by the diffusion rate, i.e. factor (iii).

It is also important to recognise that, while diffusion will be slower at temperatures between 25 °C and 80 °C, the thickness of the surface layer of titanium hydride will still increase with time. Philips [8] demonstrated that under laboratory conditions, the hydride layer thickened parabolically with time at rates of approximately 5 µm h at 80 °C and 1 µm h at 25 °C. If these rates occurred in practice over a 20 year period, a rate of 1 µm h could result in a hydride layer ~400 µm thick.

3.6.3. Hydriding from galvanic corrosion in the presence of H₂S

Published work dating to the 1950s [12–14] shows that carbon steel is likely to corrode at a higher rate when it is connected to titanium for most conditions. As with any occurrence of galvanic corrosion, the rate of corrosion will depend on the conductivity of the solution and the relative areas of titanium and carbon steel that are in contact.

Covington [10] reports that galvanic coupling of titanium and iron did not cause hydriding in clean seawater. It was their view that the electrochemical potential was not sufficient to generate hydrogen, i.e. factors (i) and (ii) in Section 3.6.2 were not satisfied. However, their experiments did demonstrate that titanium absorbed hydrogen when coupled to iron in seawater if hydrogen sulphide was present. They also stated that this mechanism explains hydriding failures of titanium tubes in sour water strippers where a galvanic couple with iron existed. No problems were reported from similar units where there was no iron.

4. Conclusions

The investigation provided clear evidence of the hazards that can arise when corrosion is not detected in complex equipment.

Failure investigation indicated that the primary stage in the failure of the heat exchanger was localised deterioration of the carbon steel tube sheet due to galvanic corrosion. Galvanic corrosion was localised where the interface between the carbon steel tube sheet and the titanium cladding sheet was exposed to corrosive condensate. Hydrogen generated by the galvanic corrosion diffused along the bond interface to form a layer of titanium hydride in the cladding.

The composition of the corrosion product indicates that the condensate in the lower area of the heat exchanger probably contained hydrogen sulphide and was therefore acidic. Published literature shows that hydrogen sulphide is a very significant factor because it increases the probability that galvanic corrosion will cause hydride formation when titanium is in contact with carbon steel.

The strength and fracture toughness of the explosive bond interface between the titanium cladding and the carbon steel tube sheet had been substantially degraded over time by the titanium hydride.
The evidence indicated that the tube bundle and bonnet probably separated due to sudden fracture of the titanium cladding from the carbon steel tube sheet. Dome shaped deformation of the dis-bonded cladding due to pressurisation would have applied leverage, which overloaded the shell retention flange.

There was no evidence to indicate failure of a tube or tube to tube sheet weld. Furthermore, these events would have been detected by the water-side hydrocarbon detection.

There was no evidence to suggest that material or manufacturing deficiencies contributed to any stages of the heat exchanger failure.

The design of the heat exchanger was such that it was susceptible to titanium hydride formation from galvanic corrosion because the interface between the titanium cladding sheet and the carbon steel tube sheet was exposed to wet corrosive conditions.

It is recommended that potential effects of galvanic corrosion and low fracture toughness are considered in both the design and the integrity management of structural components manufactured from dissimilar metals by explosive bonding.

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