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Review of external stress corrosion cracking of 22%Cr duplex stainless steel

Phase 1 – Operational data acquisition

Prepared by **TWI Ltd**
for the Health and Safety Executive 2003

RESEARCH REPORT 129

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Health & Safety
Executive

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Failure of offshore equipment leading to release of hydrocarbons has potentially serious safety, environmental and financial implications. One important source of such releases is corrosion related failures of offshore process plant. Following failures of duplex stainless steel in 2001/2002 resulting from chloride stress corrosion cracking, the Health and Safety Executive commissioned a review of the offshore operation of duplex stainless steel process plant with respect to chloride stress corrosion cracking. This report reviews the occurrence and mitigation of chloride stress corrosion cracking in the UK offshore sector, including design, fabrication, repair and operation of offshore facilities.

This report and the work it describes were funded by the Health and Safety Executive (HSE). Its contents, including any opinions and/or conclusions expressed, are those of the authors alone and do not necessarily reflect HSE policy.

HSE BOOKS

First published 2003

ISBN 0 7176 2718 7

EXECUTIVE SUMMARY

BACKGROUND

The Health and Safety Executive (HSE) has a strategy to reduce hydrocarbon releases that occur in the UK oil and gas sector. One source of such releases is corrosion related failures of equipment on offshore installations. Following failures of duplex stainless steel offshore pipework in 2001/2002 resulting from chloride stress corrosion cracking, HSE commissioned TWI to review the subject of chloride stress corrosion cracking of duplex stainless steel and to establish the state-of-the-art position on understanding the acceptable envelope of operation of the material. Two phases of the work were considered: Phase 1 – collation of data pertaining to design and operation of high pressure/high temperature facilities (i.e. generally operating above 100ºC), with a view to avoiding stress corrosion cracking, and Phase 2 – review of public domain information related to temperature limits for chloride stress corrosion cracking of duplex stainless steels and field experience. This report covers the findings of Phase 1, which specifically included obtaining practical information from the UK offshore operating sector on the occurrence and mitigation of chloride stress corrosion cracking of 22%Cr duplex stainless steel. Data relating to design, fabrication, repair and operation of such facilities were compiled and reviewed.

CONCLUSIONS

1. There is an inconsistency within the UK offshore sector concerning the temperature limits and coating practice for mitigation against external chloride stress corrosion cracking. There is a need for an agreed set of limits and guidance on design against external chloride stress corrosion cracking.

2. Internal chloride stress corrosion cracking was not anticipated because of the perceived total absence of oxygen in process fluids and a lack of knowledge at the design stage of possible conditions that could result in localised concentration of chlorides. There is a need to establish limits of temperature, chloride and cathodic reactants. The assumed absence of oxygen in process plant cannot be relied on as the sole factor in the prevention of stress corrosion cracking.

3. The variety of external experience at temperatures >100°C probably reflects the need to develop and maintain high chloride liquid with a significant time over which it wets the surface of the metal. Therefore, it is likely that the presence of a crevice, wet insulation or salt encrustation is necessary to cause a problem.

4. Coatings are relied upon to mitigate against external stress corrosion cracking of duplex stainless steels. However, these require inspection, maintenance and replacement if they are to remain effective. Although, in general, coatings do not provide 100% protection, combined with the difficulty in achieving external conditions suitable for stress corrosion cracking, they are probably an appropriate mitigation measure.

5. It is necessary that during manufacture of topside equipment, quality procedures be in place to ensure that design intent is carried though to completion.

RECOMMENDATIONS

1. There is a need to review the temperature limits and coating measures adopted by the UK offshore sector with regard to the published data (Phase 2 of the current work), to establish agreed working limits and to develop design guidance with respect to the avoidance of crevices, damaging deposits and optimum coatings.

2. The mechanism of cracking of duplex stainless steel in exotic brines, in the absence of appreciable levels of oxygen, should be investigated. This should include investigation of the effects of pH, chloride concentration, temperature and H_2S content.

3. The limits of temperature and chloride content responsible for internal chloride stress corrosion cracking of duplex stainless steel in the absence of oxygen should be determined.

4. There is a need to establish best practice NDT techniques for detecting stress corrosion cracks and inspection of duplex stainless steel process plant generally within overall corrosion management systems and schemes.

5. Designers need to consider the potential range of conditions that could occur in process plant at the design stage in order to make the appropriate material selection. This is particularly the case at points of pressure/temperature and process fluid changes.

6. The reliability of TSA coatings with organic coatings/sealants to protect duplex stainless steel on topside structures should be evaluated, eg to establish whether they provide galvanic protection in addition to a physical barrier.

1. INTRODUCTION

1.1 BACKGROUND

The Health and Safety Executive (HSE) has stated that over the period 1993-2001, about 350 hydrocarbon releases were reported in the UK oil and gas sector that were attributed to corrosion and related materials failure events on offshore process plant. This figure represented about 15-20% of the total number of reported releases for the period (1). Whilst the figure attributed solely to corrosion over the period 1999-2001 was lower than this, between ~6% and ~12%, the trend was of an increase in corrosion related failures and subsequent hydrocarbon releases (2). Equipment failure leading to release of hydrocarbons not only incurs a financial impact due to loss in production, but also impacts adversely on the environment and of most importance, places at risk the safe operation of offshore facilities. Of particular concern are those instances in which releases may occur from high pressure/high temperature (HP/HT) facilities.

Following failures of duplex stainless steel offshore pipework in 2001/2002 resulting from chloride stress corrosion cracking at elevated temperature, HSE commissioned TWI to review the subject of chloride stress corrosion cracking of duplex stainless steel and to establish the state-of-the-art position on understanding the acceptable envelope of operation for the material. This was part of HSE's strategy to reduce, by 2004, hydrocarbon releases to 50% of the 1999/2000 level. Two phases of the work were considered: Phase 1 – collation of data pertaining to design and operation of HP/HT facilities (i.e. generally operating at temperatures in excess of 100ºC) with a view to avoiding chloride stress corrosion cracking and Phase 2 – review of public domain information related to temperature limits for chloride stress corrosion cracking of duplex stainless steel and field experience. This report covers the findings of Phase 1, which specifically included obtaining practical information from the UK offshore operating sector on the occurrence and mitigation of chloride stress corrosion cracking of 22%Cr duplex stainless steel. Data relating to design, fabrication, repair and operation of such facilities was compiled and reviewed.

1.2 DUPLEX STAINLESS STEELS AND STRESS CORROSION CRACKING

The term "duplex stainless steel" refers to the family of stainless steels that possess a two-phase structure of delta ferrite and austenite. This family of alloys has achieved widespread industrial application, including in the offshore oil and gas sector, due in part to an attractive combination of higher strength and improved stress corrosion cracking resistance compared with austenitic stainless steels. Specific alloys are sometimes described by their chromium content as either 22%Cr "duplex" or 25%Cr "superduplex" grades, although a stricter definition of the latter category is those alloys possessing a Pitting Resistance Equivalent number (PRE_N) greater than 40. The reader is directed to reference 3 for a more detailed description of specific grades and their properties.

Stress corrosion cracking is a term applied to failures that occur in alloys by the propagation of cracks in a corrosive environment (4). It requires the presence of a stress, either residual, applied, or present in combination, a specific corrodent and a susceptible material. Duplex stainless steels are known to be susceptible to stress corrosion cracking in chloride-containing environments (4,5). Indeed, some standards, such as NORSOK (6) specify temperature limits for unprotected duplex (100°C) and superduplex (110°C) stainless steels that operate in salt-laden environments.

2. SERVICE FAILURES OF DUPLEX STAINLESS STEELS ATTRIBUTED TO CHLORIDE STRESS CORROSION CRACKING

2.1 INTRODUCTION

In reviewing the design and operation of offshore facilities using duplex stainless steel it is worth commenting on the failures of duplex stainless steel that have been attributed to chloride stress corrosion cracking. The majority of those presented relate to UK offshore experience. Except where the information has already been published in the public domain, details of specific operators have not been included.

2.2 EXTERNAL STRESS CORROSION CRACKING

A number of service failures have occurred that have been attributed to external chloride stress corrosion cracking. Table 1 summarises the reported conditions for each of the incidents. Failure under wet insulation was reported in two instances: the first involved a 22%Cr duplex stainless steel (UNS S31803) separator after 18 months operation between 40°C and 100ºC, failure being attributed to poor welding practice (the presence of hydrogen cracks) and a high weld metal ferrite content (>70%) (3); the second instance occurred under wet insulation on a superduplex stainless steel manifold, manufactured via a powder metallurgy route and operating at ~100ºC, in which surface crazing was detected in the weld heat affected zone (HAZ) during routine inspection. No leak was detected in this second example; the cracks were reported to have been ground out and weld repaired. Following this, the surface of the manifold was painted before reinstating the insulation. The regions that had exhibited cracking were left uninsulated to permit periodic non-destructive examination using an ACFM technique. The insulation was coated with a watertight seal to prevent any further soaking; no further cracking was reported.

Two instances were reported of chloride stress corrosion cracking of duplex stainless steel that was not insulated. The first concerned a 22%Cr duplex stainless steel heat exchanger which operated with a gas inlet temperature of ~160ºC and an outlet temperature of ~46ºC. Regular seawater deluge and dripping water from overhead pipework and walkways produced salt encrustation on the inlet header; cracking then occurred beneath the salt deposit in the weld HAZ at the inlet header. The stress driving the stress corrosion cracking was attributed to a combination of welding residual stress and thermal stress. Subsequent investigation also identified significant loading of the heat exchanger headers due to inadequate pipe supports. In this instance, mitigation against a further occurrence of cracking was achieved by the application of a thermally sprayed aluminium (TSA) coating. Regular inspection since the incident has not identified any further cracking. The second instance involved a 22%Cr separator, which operated at 105°C. Cracking occurred as a result of seawater dripping onto an unprotected surface.

The final instance of external stress corrosion cracking, which was actually a series of cracks in the same unit, was reported to have occurred from crevice regions within trunnion supports on type UNS S31803 22%Cr duplex stainless steel spool pieces operating at 140ºC. In these instances, the external surfaces of the spool pieces were coated with a two part epoxy-based paint. The interior surfaces of the trunnions were unpainted and the weep hole in each trunnion had not been plugged, which was contrary to the design intent. Thus, the marine environment had access to the unpainted duplex stainless steel. Cracking was again associated with the weld HAZ region and was detected originally by personnel who observed the weeping of condensate.

Table 1 Summary of examples of failures attributed to stress corrosion cracking

Equipment	*Internal/ External*	*Temperature, ºC*	*Grade*	*Comments*
Separator	External	40-100	22%Cr	Under wet insulation. Failure attributed to poor welding practice and high weld metal ferrite content
Separator	External	105	22%Cr	Dripping seawater onto unprotected surface
Manifold	External	~100	25%Cr	Under wet insulation. Cracking in weld HAZ
Heat exchanger	External	~160	22%Cr	Uncoated, subject to regular seawater deluge
Spool pieces, trunnion supports	External	140	22%Cr	Internal surfaces of trunnions unpainted. Chloride-containing environment gained access via unplugged weep holes in trunnions
Downhole tubing	Internal	~170	25%Cr	Chloride level not known, but it was believed that oxygen ingress had occurred
Spool piece	Internal	140	22%Cr	Chloride concentration as a result of a pressure drop across a level control valve. Oxygen believed to be absent
Spool piece	Internal	120	22%Cr	Chloride concentration as a result of a pressure drop across a level control valve. Oxygen believed to be absent

2.3 INTERNAL STRESS CORROSION CRACKING

In addition to failures attributed to external chloride stress corrosion cracking, two failures were reported to have occurred as a result of internal chlorides in process pipework (Table 1). These failures occurred in 22%Cr duplex stainless steel operating at 140ºC and 120ºC respectively. In both instances, failure occurred under highly localised conditions, in which all of the factors necessary for stress corrosion cracking occurred. The chloride concentration is believed to have occurred due to the flashing-off of water at a level control valve, raising the chloride concentration to the level of “exotic brines” from 200g/l to >400g/l in the first failure, with a substantial level of $MgCl_2$ being reported. The presence of a suitable cathodic reactant remains a subject of some debate. In both instances, oxygen was believed to be absent. However, in the case of the former failure, subsequent laboratory tests were reported to have induced cracking in 22%Cr duplex stainless steels at 140ºC, in simulated service brine with 450g/l chloride, in the absence of oxygen. Indeed, cracking was also reported in superduplex stainless steel under these conditions (7). Oxygen, by its nature, is difficult to exclude from process plant and laboratory tests. However, the results do indicate that there is no place for an argument for a "threshold" level, below which cracking will not occur.

One instance of chloride stress corrosion cracking also in ostensibly deoxygenated conditions was reported for superduplex stainless steel downhole tubulars. Cracking occurred at a temperature of ~170ºC. The chloride level was not known. However, in this instance, it was concluded that oxygen ingress had occurred which led to cracking, either due to inadvertent air ingress or oxygen present in additives to the completion brine, notably the corrosion inhibitor.

3. DESIGN AND SERVICE PRACTICE IN MITIGATING AGAINST CHLORIDE STRESS CORROSION CRACKING

3.1 EXTERNAL STRESS CORROSION CRACKING

Table 2 summarises some of the UK practice in the use of duplex stainless steel on topsides in terms of typical temperatures of operation and the types of measures taken, if any, to mitigate against external chloride stress corrosion cracking. In general, temperatures of operation and internal process conditions are derived from well conditions and predictive models. Whilst internal process stream temperatures may be monitored, such information is not available at the design stage; external temperature monitoring of process plant surfaces may not be performed. Similarly, at the design stage, theoretical judgements are made regarding process stream conditions; often, the effects of changes in pressure/temperature and process fluid or upset conditions may not be accounted for. Mitigation measures may be divided into three groupings: use of paint systems, use of TSA, or no coating of any kind. Two separate issues regarding coating application are encountered at the design stage. The first is a reluctance to rely on a coating as the only mitigation method to prevent stress corrosion cracking; should the coating integrity be lost, the material is at risk of cracking. As a result, some designers prefer to use coatings as only an additional protection after selecting a material that is resistant to stress corrosion cracking under the expected operating conditions, ie a “belt and braces” approach is adopted. The second issue encountered is an erroneous opinion that corrosion resistant alloys, such as duplex stainless steel, do not require any form of corrosion protection, ie that they are “stainless” and so will not corrode under any conditions. It may be noted that coatings are not only applied to mitigate against external stress corrosion cracking; they are also applied to protect the steel against pitting and crevice corrosion, and for this reason, application of coatings even in relatively low temperature environments, say 50°C, may be advantageous.

The selection of a mitigation method also depends on whether equipment is thermally insulated. For example, most operators will coat any duplex stainless steel that is to be insulated, and some operators coat all duplex stainless steel operating above 50ºC, regardless of whether it is insulated or not. Others will only coat uninsulated duplex stainless steel if it operates above 120ºC.

It was reported that some 22%Cr pipes were left uncoated when operating above 50ºC, examples were cited of operation at 60-70ºC, 75-80ºC and above 100ºC (but below 140-150ºC); there was also a report of flowlines operating at 140-150ºC elsewhere in the world that were uncoated. In each of these instances, the flowlines were encrusted with salt and there had been no reports of failures. In some of these instances, piping was supported without protection against crevice corrosion; even under these conditions, problems of crevice corrosion were not reported. It may be noted that there is a trend to only insulate duplex stainless steel for heat retention purposes. Where personal protection is required, cages are preferred, as this renders the equipment easier to inspect and removes any possibility of having wet insulation. The use of thermal insulation presents practical difficulties to the operator. It is essential that the insulation be kept dry to prevent stress corrosion cracking of the hot duplex stainless steel, or indeed corrosion under insulation (CUI). However, it is necessary to test regularly fire protection systems and in doing so demonstrate that the system will effectively deluge the insulated equipment with water. Even with the use of waterproof coatings on the insulation, most operators acknowledge the risk of it being soaked with water.

The requirements of fire system testing and the risk to equipment posed by the test are areas of concern to many operators.

Table 2 Summary of examples of coating practice for duplex stainless steel

Example	*Temperature, ºC*	*Uninsulated*	*Insulated*
1	<120	Uncoated	Epoxy phenolic paint
	>120	TSA and silicone	TSA and silicone
2	≤50	Uncoated	Glass flake epoxy paint Polyamide cured epoxy paint Epoxy and high gloss acrylic paint Epoxy phenolic paint
	51 to ≤120	Glass flake epoxy paint Polyamide cured epoxy paint Epoxy and high gloss acrylic paint Epoxy phenolic paint	Glass flake epoxy paint Polyamide cured epoxy paint Epoxy and high gloss acrylic paint Epoxy phenolic paint
	>120	Heat resistant silicone paint Heat resistant silicone aluminium pigmented paint Modified polysiloxane resin based paint	Heat resistant silicone paint Heat resistant silicone aluminium pigmented paint Modified polysiloxane resin based paint
3	100<T<140	Uncoated	-
	140-150	TSA	TSA
4	≤80	Uncoated	Coated *
	>80	Coated*	Coated *

** TSA on manifolds, remainder epoxy-based paint system*

A range of practice exists regarding the choice of coatings employed on duplex stainless steel; Table 3 summarises some of the common systems adopted by UK operators. These include: organic paint systems, eg glass flake epoxy, silicone, acrylic, polysiloxane and epoxy-phenolic, some of which include aluminium pigmentation, and TSA. The latter is generally employed with an organic paint system final coat. Of note with the organic paint systems is that several require curing at around 200°C, although some, such as the silicone type, do "harden" at ambient temperature. In most cases curing is not performed at application. Instead, reliance is made of curing in service, which is typically less that 200°C for duplex stainless steel applications. Therefore, although some curing may be expected to occur during service, optimum-coating properties may not be achieved. In addition, most coating systems have an operational life less than the underlying substrate. Consequently, consideration must be given to the need to repaint, often in situ, over the design lifetime. Some coatings may be repainted; others must be removed before reapplication. TSA coatings have the potential to be more maintenance-free than organic coatings. Not only do they provide a physical barrier to corrosive species reaching the substrate, but if damaged, in the presence of an electrolyte they might also provide a degree of cathodic protection. The use of TSA coatings remains in its infancy and limited long-term data is available; research is proposed to understand its long-term behaviour. What performance data is available is anecdotal and not rigorous. Concern remains over the possibility of unprotected areas remaining, such as inside trunnions, which were responsible for some of the reported failures.

Table 3 Typical coating systems used on duplex stainless steel

Coating type	*Temperature limit, notes*
Epoxy base	Various types, including epoxy phenolics and may contain glass flakes. Typically used as a primer as they usually require a top coat that has UV resistance. Used up to 100-150°C.
Silicone base	May require curing at 200°C. Several types, eg: - siloxane variants used up to 450°C. - silicone aluminium can be used up to 540°C, but this is dependent on the primer. - silicone acrylic can be used up to 600°C as a top coat, but limited to 400°C in combination with zinc silicate primers.
Acrylic base	Provide a gloss finish and are used for top coats.

3.2 INTERNAL STRESS CORROSION CRACKING

Following the recent failures attributed to internal chloride stress corrosion cracking, considerable concern now exists in the industry concerning the possibility of further occurrences. At the design stage, materials are selected, amongst other considerations, on their ability to withstand well fluids. If necessary, corrosion tests will be performed in simulated production chemistries. However, upset or local conditions are rarely considered. In the case of the recent topside pipework failures, chloride concentration occurred due to flashing-off of water at a level control valve. The role of oxygen in the failures remains open to debate. Recent tests have demonstrated that duplex stainless steel may crack in oxygen-free solutions at 140°C containing 450g/l chloride with substantial levels of $MgCl_2$. However, for the purposes of future design, the threshold levels of chloride and the relevant cations and their temperature dependence in deoxygenated environments needs to be determined. Also, the actual mechanism of cracking under these conditions is not known, for example the role of alternative cathodic reactants such as hydrogen sulphide, if any, under these conditions remains unclear.

What has emerged from this experience is the need to appreciate and consider all factors that may occur in process plant and to define as much as possible the actual operating conditions. On the basis of these, materials testing may then be required, as far as is possible, in the range of conditions that most realistically reflects actual operation. Consideration must also be given to how process conditions may change during the lifetime of the plant.

4. NON DESTRUCTIVE EXAMINATION OF DUPLEX STAINLESS STEEL FOR STRESS CORROSION CRACKING

Inspection for stress corrosion cracking has generally relied on a philosophy of prevention rather than detection. Stress corrosion cracking can occur with little warning and over a relatively short time interval. Hence, inspection cannot be relied upon to detect cracking prior to failure. Most inspection techniques have been directed towards coating examination for pinholes, damage, degradation etc. In the majority of the instances of failure, detection was made visually by personnel. Most operators who have developed, or are in the process of developing, non-destructive examination techniques, have done so after experiencing stress corrosion cracking failures. In these instances, inspection has concentrated on specific areas of risk, ie areas of high stress at welds etc. In such circumstances, the aim is to identify whether any other equipment is at risk. Two techniques have been utilised: ACFM and acoustic emission. Some operators have reported satisfaction with ACFM for the regular monitoring of particular vessels. It is understood that acoustic emission remains under trial. The presence of TSA coatings on duplex stainless steel has been raised by some operators as a hindrance to successful inspection, particularly where ultrasonic probes are permanently attached for sand erosion monitoring. Under such circumstances, removal of the protective coating has been necessary. It should be noted that such “high temperature” non-destructive testing presents its own safety concerns. By nature of the application, personnel safety protection has to be removed from hot equipment.

5. DISCUSSION

5.1 FACTORS CONTROLLING STRESS CORROSION CRACKING

In simple terms, stress corrosion cracking may be thought of as occurring by the combined action of three main factors: the presence of a stress, a susceptible material and a corrosive environment. In addition to these, both temperature and time play an important role in determining if cracking will occur. If any one of these main factors is removed, stress corrosion cracking will not occur. Considering first the presence of stress: in theory, if the stress is maintained below a level known to provide no risk of cracking, equipment will be safe. However, the stress component will include not only service loading, but also include stress from manufacture. Whilst the former may be relatively easily determined and controlled, the latter is considerably more difficult to limit or remove. For example, welding residual stresses are conservatively regarded as being tensile and of proof strength magnitude; they may be reduced by appropriate heat treatment, although for many applications, this is impractical. Indeed, most reported failures of duplex stainless steel components appear to have occurred at regions associated with welding, in particular in the HAZ. In the case of duplex stainless steels, postweld heat treatment would create the risk of intermetallic phase formation, with consequential reduction in both toughness and corrosion resistance. Therefore, postweld heat treatment must be viewed with caution, as the problems created by it may be as great as the stress corrosion cracking it was trying to resolve. In some components, such as spool pieces manufactured from a number of components comprising wrought pipe and forged flanges and fittings, it is conceivable that these could be manufactured, either from component parts by welding or by a single powder metallurgy route and hot isostatically pressed, followed by heat treatment at the solution annealing temperature. Whilst most residual stresses are relieved at the solution annealing temperature, slow cooling would be required to avoid reintroducing them; in practice, rapid water quenching is necessary to prevent intermetallic phase precipitation, which would result in the reintroduction of residual stresses. Any duplex stainless steel component is likely to contain residual stresses as a result of quenching following a solution annealing heat treatment.

The second requirement for stress corrosion cracking is a susceptible material or microstructure. Most cases of external stress corrosion cracking of duplex stainless steels have been associated with the weld HAZ. A feature of the HAZ is that its microstructure is different to that of the parent metal. Whereas the parent metal, be it wrought tube, plate or forging, will typically contain around 50% austenite and 50% ferrite, the HAZ will generally contain a greater volume fraction of ferrite, up to 70% being permitted in some specifications. It is known that the microstructure of duplex stainless steels is responsible for much of their superior corrosion and stress corrosion cracking performance in chloride containing environments compared with their austenitic stainless steel counterparts. Parent metal and weld/HAZ microstructures are specified within certain tolerances. In only one reported instance was poor weld microstructure implicated in a failure, in which the weld metal ferrite content was reported to be too high. In most HAZ failures it is not possible to separate the effects of different local microstructure and residual stress as contributory factors.

Finally, the environment, in terms of the presence of a suitable electrolyte, chlorides, a cathodic reactant (usually oxygen) and temperature, contributes to cracking. Deposits or crevices may allow solutions with high $MgCl_2$ content to remain above 100°C. At very high temperatures, the problem may be eliminated because the duration during which the metal surface is wet is too short for crack initiation. Internally, high pressures will maintain liquid containing high concentrations of chloride at high temperatures, therefore, potentially, there is less need for crevices or deposits. Theoretically, it may be preferable to reduce the temperature to avoid cracking. However, in many cases, operational factors limit the ability to control temperature. Most UK experience of mitigating against stress corrosion cracking is concerned with taking action against all of these environmental factors being present at the same time.

5.2 UK EXPERIENCE

Review of service experience with duplex stainless steels in relation to chloride stress corrosion cracking highlights a number of similarities and differences in the approaches adopted by UK North Sea operators. Two principal approaches appear to be adopted: in situations where the temperature is, or may be maintained below a level that is deemed to be the limit for stress corrosion cracking, the material is operated without a coating; where the temperature is above this limit, duplex stainless steel may still be selected as the material of choice for the application, but a coating will be applied. The reported incidences of failure under wet insulation of uncoated duplex stainless steel have led to a largely consistent approach of coating any metal surface that is to be insulated, irrespective of the actual operating temperature. Where differences do exist, these are primarily with the choice of coating system. For example, some operators specify TSA coatings regardless of temperature, whereas others specify paint systems, or a combination of paint systems and TSA depending on the operating temperature.

Where practice varies most noticeably is in relation to uninsulated duplex stainless steel. Some uninsulated flowlines operate up to 120ºC, although this is likely to be an internal process fluid temperature rather than the temperature of the surface of the pipe. In one instance flowlines reportedly operate up to ~140ºC, without a protective paint or TSA coating, and were reported to be encrusted with salt deposits. Other operators apply a protective coating to uninsulated duplex stainless steel operating above 80ºC or even 50ºC. The variation in practice indicates some uncertainty in the industry concerning the actual temperature limits for external chloride stress corrosion cracking. Failures as a result of dripping water containing chloride leading to salt build up and chloride concentration were reported to have occurred at temperatures as low as 105ºC in one instance, although others occurred at ≥140ºC. This suggests that coating duplex stainless steel at temperatures above say 80ºC would be prudent, with 50ºC being over conservative, although, the service experience of failure under insulation at a temperature between 40°C and 100°C would explain this approach. Also, it would indicate that leaving unprotected duplex stainless steel at 120ºC would be in contradiction of failure experience. However, there is also considerable field experience of uncoated duplex stainless steel operating above 100ºC, with salt encrustation, that has not cracked. The critical factor here would appear to be whether the surface of the steel remains wet beneath the salt encrustation and in areas of high stress. Presumably, failures occurred under conditions in which the steel was repeatedly wet; service experience of an absence of failures despite salt encrustration implies that the crust must be of sufficient thickness that the steel surface remains dry, or that wetting is infrequent, effectively lengthening the crack initiation period. It may be that given extended exposure, these conditions could eventually lead to cracking. Also, operational conditions change, perhaps leading to falling temperatures; conditions for stress corrosion cracking may then be encountered in the future.

Experience of the UK operating sector would indicate that the temperature limits for the safe operation of duplex stainless steel for different operating conditions are not well defined. It is recognised that temperature limits are provided by some standards, such as NORSOK, for the external exposure of unpainted stainless steels in a marine environment, and indeed, most companies operate with their own limits. In the case of NORSOK, the limit for 22%Cr duplex stainless steel is 100°C, which has been recently revised down from 110°C, as has the limit for superduplex stainless steel (from 120°C to 110°C). Some successful experience has been achieved above this limit. However, failures have also occurred close to the limit. It may be hypothesised that different temperature limits may exist for aerated (external) conditions and for deaerated (internal) conditions. Within each of these cases, the temperature limit may be further affected by chloride level (and also the type of cation, which influences the potential), and the period over which wetting occurs. If external surfaces of duplex stainless steel are very hot, the period of wetting may be very short, effectively increasing the initiation period for cracking. The worst case may be at temperatures just above 100°C, where the metal surface may remain in contact with hot chloride solution for an extended period of time. Magnesium ions are considered particularly detrimental with respect to stress corrosion cracking of duplex stainless steel and $MgCl_2$ in solution can raise the boiling point of water to well above 100°C.

When a coating system is selected, a number of other factors must be considered. A feature of several of the epoxy or silicone resin based paint systems in use as corrosion protection on duplex stainless steel structures is that they require curing at an elevated temperature, typically 200°C to achieve optimum properties. Most coated duplex stainless steel operates at temperatures below 200°C, so operating conditions cannot be relied upon to achieve effective curing of the paint. It is unclear if many painted components ever receive the manufacturers' curing treatment prior to service. Another feature of any coating system is the necessity to maintain coating integrity over the life of the equipment; indeed, detection of coating "holidays" even after application can be problematic and complete cover can not always be guaranteed. Offshore structures may have design lives of 20-25 years, whereas most paint-based coatings will typically require re-application after ten years in operation. In addition, regular inspection is required to check for damage or coating degradation. It is questionable whether operators can rely on 100% protection with any organic paint based coating system.

The recent experience of internal chloride stress corrosion cracking in duplex stainless steel in the apparent absence of oxygen is a significant development. Recent tests have demonstrated that under the apparent local operating conditions cracking could be reproduced. However, there is a need to understand both the mechanism and the interplay of factors such as temperature, chloride concentration, pH etc and potentially alternative cathodic reactants in defining operating conditions for the safe use of duplex stainless steels. Furthermore, the incidences highlight the need to understand the local conditions that may be generated internally in production equipment during operation. Following recent experience, it should be accepted that simple reliance on the absence of oxygen to avoid stress corrosion cracking in process plant is not possible.

6. CONCLUSIONS

Following a review of current practice and experience of the use of duplex stainless steels in the UK offshore operating sector, the following conclusions may be drawn:

1. There is an inconsistency within the UK offshore sector concerning the temperature limits and coating practice for mitigation against external chloride stress corrosion cracking. There is a need for an agreed set of limits and guidance on design against external chloride stress corrosion cracking.

2. Internal chloride stress corrosion cracking was not anticipated because of the perceived total absence of oxygen in process fluids and a lack of knowledge at the design stage of possible conditions that could result in localised concentration of chlorides. There is a need to establish limits of temperature, chloride and cathodic reactants. The assumed absence of oxygen in process plant cannot be relied on as the sole factor in the prevention of stress corrosion cracking.

3. The variety of external experience at temperatures >100°C probably reflects the need to develop and maintain high chloride liquid with a significant time over which it wets the surface of the metal. Therefore, it is likely that the presence of a crevice, wet insulation or salt encrustation is necessary to cause a problem.

4. Coatings are relied upon to mitigate against external stress corrosion cracking of duplex stainless steels. However, these require inspection, maintenance and replacement if they are to remain effective. Although, in general, coatings do not provide 100% protection, combined with the difficulty in achieving external conditions suitable for stress corrosion cracking, they are probably an appropriate mitigation measure.

5. It is necessary that during manufacture of topside equipment, quality procedures be in place to ensure that design intent is carried though to completion.

7. RECOMMENDATIONS

1. There is a need to review the temperature limits and coating measures adopted by the UK offshore sector with regard to the published data (Phase 2 of the current work), to establish agreed working limits and to develop design guidance with respect to the avoidance of crevices, damaging deposits and optimum coatings.

2. The mechanism of cracking of duplex stainless steel in exotic brines, in the absence of appreciable levels of oxygen, should be investigated. This should include investigation of the effects of pH, chloride concentration, temperature and H_2S content.

3. The limits of temperature and chloride content responsible for internal chloride stress corrosion cracking of duplex stainless steel in the absence of oxygen should be determined.

4. There is a need to establish best practice NDT techniques for detecting stress corrosion cracks and inspection of duplex stainless steel process plant generally within overall corrosion management systems and schemes.

5. Designers need to consider the potential range of conditions that could occur in process plant at the design stage in order to make the appropriate material selection. This is particularly the case at points of pressure/temperature and process fluid changes.

6. The reliability of TSA coatings with organic coatings/sealants to protect duplex stainless steel on topside structures should be evaluated, eg to establish whether they provide galvanic protection in addition to a physical barrier.

8. ACKNOWLEDGEMENTS

The author thanks the members of the UK offshore operating sector for providing information for the review. The assistance of colleagues at TWI Ltd is gratefully acknowledged.

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