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Chloride stress corrosion cracking of duplex stainless steels in the absence of oxygen

Phase two - Electrochemical monitoring of SCC

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Chloride stress corrosion cracking of duplex stainless steels in the absence of oxygen

Phase two - Electrochemical monitoring of SCC

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Failure of offshore equipment leading to release of hydrocarbons has potentially serious implications and early detection is fundamental to reduce the risk and prevent costly and, in some cases potentially catastrophic events. 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 what experimental techniques and what commercially available technologies may be applicable to monitoring duplex stainless steel process plant operating at high temperature.

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EXECUTIVE SUMMARY

BACKGROUND

The Heath and Safety Executive (HSE) has a strategy to reduce the incidence of hydrocarbon releases in the UK oil and gas sector. One source of such releases is corrosion related failure of equipment. Following offshore incidents associated with stress corrosion cracking (SCC) of 22%Cr duplex stainless steels (DSS), HSE commissioned TWI to review current practice within the UK offshore sector with respect to chloride stress corrosion cracking of these alloys. Phase I of this work (1) compiled and reviewed data and practical information relating to design, fabrication, repair and operation of DSS high pressure/high temperature facilities (i.e. operating above 100ºC), with a view to avoiding SCC. One of the conclusions from this work was that internal chloride stress corrosion cracking had not been anticipated because of the perceived total absence of oxygen in process fluids. It was recognised that early detection is fundamental to reduce the risk of failure and prevent costly and, in some cases potentially catastrophic events. This report comprises Phase II of the work commissioned by HSE to investigate the chloride SCC of 22%Cr DSS via a review exercise to determine what experimental techniques and what commercially available technologies may be applicable to monitoring process plant operating at high temperature. Relevant published literature was reviewed and additional information was obtained from discussions with other corrosion experts in the field.

CONCLUSIONS

1. There are no laboratory or industrially proven solutions for electrochemical monitoring of internal stress corrosion cracking in duplex stainless steels, but several technologies have been the subject of promising laboratory trials for other materials.

2. The principal techniques available for real-time monitoring of internal corrosion in stainless steel process pipework, i.e. electrical resistance and linear polarisation resistance, give poor correlation with localised corrosion and are not suitable to monitor chloride stress corrosion cracking alone.

3. Electrochemical noise monitoring has been used in assessing both general corrosion and localised corrosion phenomena in laboratory and plant for a range of materials. Whilst data specific to duplex stainless steel are not available, it is probably the best candidate direct electrochemical method for detecting and monitoring localised corrosion in stainless steels.

4. In cases where the SCC controlling parameters are well understood and the envelope for safe conditions has been established, then a monitoring approach could be considered, based on the on-line measurement of the process variables, assuming that the material is inherently susceptible to SCC.

5. It is possible that one technique in isolation may be capable of monitoring SCC in duplex stainless steels, but it is more likely that a combined electrochemical/environment/non-destructive evaluation strategy will be required to mitigate the risk of failure.

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(1) Leonard A J: 'Review of external stress corrosion cracking of 22%Cr duplex stainless steel. Phase 1 – Operational data acquisition'. HSE Research Report no.129, 2003. Publ: HSE, Norwich, UK, 2003. ISBN 0717627187

6. There are no laboratory or industrially proven solutions for electrochemical monitoring of external stress corrosion cracking.

7. There are many practical difficulties in electrochemical monitoring external SCC, but use of a modified probe, fitted with a means of retaining salt on the surface whilst allowing water permeation, may allow the assessment of salt cake or saturated solution conditions.

8. Given the practical difficulties associated with electrochemical methods as applied to external SCC, then a monitoring approach should be developed, based on the on-line measurement of critical variables, assuming that the material is inherently susceptible to SCC. Measurement locations could be modified to replicate worst-case conditions for inaccessible locations on site.

RECOMMENDATIONS

Given the safety advantages of pre-empting the on-set of SCC, as opposed to post-crack detection, it is recommended that the most promising techniques identified in the present work be developed further and that guidelines be produced for their industrial application. It is recommended that the following items be addressed by industry:

Monitoring of Environment

- Definition is required of industrially relevant environmental parameter envelopes in which the likelihood of SCC of welded duplex stainless steels is significant. This should be established by review of existing data and experience, and specific laboratory testing.
- Commercial environmental monitoring systems should be assessed for their ability to accurately determine if conditions change to within the critical envelope. Location of such monitoring devices will be significantly influenced by process stream knowledge and/or modelling to identify areas where the likelihood of SCC is greatest.

Monitoring of Materials Response

- Electrochemical noise monitoring in isolation and in combination with other techniques should be developed further for application to duplex stainless steels. Laboratory trials will be necessary to develop and implement a practical monitoring solution for in-situ application.
- Appropriate long-life probes, including the incorporation of stressed specimens, should be assessed/developed.

Incorporation into a SCC Management Strategy

- All techniques need to be assessed in terms of variation in response with process changes, susceptibility to extraneous signals etc and correlated with the impact of system upset and initiation of SCC.
- The use of in-situ monitoring needs to be incorporated into a risk based inspection strategy, incorporating appropriate NDE as a response to any indication that the likelihood of SCC has risen above a critical level.
- Ultimately, for plant processes that necessarily operate in regimes known to present a significant threat of stress corrosion cracking to duplex stainless steels, serious consideration should be given to means of providing surface protection or even use of alternative materials in high risk areas.

1. INTRODUCTION

1.1. BACKGROUND

The Heath and Safety Executive (HSE) has a strategy to reduce the incidence of hydrocarbon releases in the UK oil and gas sector (1). One source of such releases is corrosion related failure of equipment. Following offshore incidents associated with stress corrosion cracking (SCC) of duplex stainless steels (DSS), HSE commissioned TWI to review current practice within the UK offshore sector with respect to chloride stress corrosion cracking of these alloys. Phase I of this work (2) compiled and reviewed data and practical information relating to design, fabrication, repair and operation of 22%Cr duplex stainless steel high pressure/high temperature facilities (i.e. operating above 100ºC), with a view to avoiding chloride stress corrosion cracking. One of the conclusions from this work was that internal chloride stress corrosion cracking had not been anticipated because of the perceived total absence of oxygen in process fluids. It was recommended that the mechanism of such cracking, in exotic brines, in the absence of appreciable levels of oxygen, should be investigated. Further, there was a need to establish the limits of temperature and chloride concentration responsible for such cracking.

It is therefore recognised that industry needs to develop design guidance and monitoring systems to reduce the likelihood of any future failures through "normal" SCC and that associated with high temperature exotic brines.

Early detection is fundamental to reduce the risk of failure and prevent costly and, in some cases potentially catastrophic events. An HSE survey (1) made an attempt to identify a means of safeguarding against hydrocarbon release. Inspection/monitoring was identified in nearly a third of all incidents as inadequately applied and one in ten incidents had corrosion/erosion monitoring as a failed safeguard, suggesting that checking and maintaining the condition of the plant was one of the most important ways of preventing failures and leaks. There are several test methods that can be used to assess corrosion of stainless steels, including electrochemical techniques and NDE inspection. However, there is little information regarding the feasibility of using electrochemical measurement techniques in operating process equipment to determine the likelihood of chloride stress corrosion cracking of duplex stainless steel pipework. Similarly, other techniques may provide a means of assessing the incidence of conditions conducive to the initiation of SCC. In other words, monitoring the conditions rather than the metal.

This report comprises Phase II of the work commissioned by HSE to investigate the chloride SCC of 22%Cr DSS via a review exercise to determine what experimental techniques and what commercially available technologies, may be applicable to monitoring duplex stainless steel process plant operating at high temperature. Recommend actions, where necessary, that should be taken to develop and/or prove robust monitoring solutions were also provided.

1.2. WORK CARRIED OUT

To determine the feasibility of using electrochemical techniques to assess and monitor the likelihood of SCC of duplex stainless steels, a literature search was carried out employing databases available to TWI and relevant papers were selected for review based on the relevance of the abstract. Keywords associated with 22%Cr duplex stainless steels, chloride stress corrosion cracking, electrochemical monitoring, electrochemical potential, detection, measurement, and sensors were used in the search terms. Abstracts were obtained from the following databases:

‘Weldasearch’	TWI
‘Metadex’	Cambridge Scientific Abstracts (CSA)
‘Corrosion’	Cambridge Scientific Abstracts (CSA)
‘Compendex’	Elsevier Engineering Information Inc (EEI)
‘NTIS’	National Technical Information Service (NTIS), US Department of Commerce
‘Energy’	US Department of Energy (USDOE)
‘TEMA’	FIZ Technik e.V.

Published literature was reviewed and additional information was obtained from the references cited within the papers selected for review along with comments and suggestions from discussions with other corrosion experts in the field, including corrosion engineers and metallurgists at CAPCIS and NPL.

2. MONITORING OF SCC IN DUPLEX STAINLESS STEELS

2.1. GENERAL CONSIDERATIONS

Inspection for stress corrosion cracking generally relies on a philosophy of prevention rather than detection, but inspection is necessary to demonstrate freedom from occurrence. Stress corrosion cracking can occur with little warning and failure can develop in a very short time for mechanisms with rapid propagation rates. Hence, present inspection technology that is based on intermittent examination cannot be relied upon to detect chloride SCC in stainless steels prior to failure unless initiation is earlier than the scheduled inspection, but propagation is later! However, this area is the subject of a separate Joint Industry Project at TWI (including HSE support) which commenced in September 2004 (3).

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 high likelihood of occurrence, i.e. areas of high stress at welds, aiming to identify whether any other equipment is therefore at a high level of risk. An example is acoustic monitoring, where cracking generates noise that is picked up and recorded by sensors.

Monitoring methods for estimating whether an environmental condition satisfies a critical one for the initiation and propagation of SCC, are usually based on electrochemical techniques. Electrochemical techniques measure electrochemical potentials and/or currents to monitor material response to the environmental conditions. This can be the response of specimens representative of the plant material, or electrodes responding to changes in the environment (redox measurements).

In addition, if the mechanism and governing parameters are well defined, it is feasible to consider monitoring the key variables to ascertain whether the environment has entered a condition likely to lead to SCC. Such changes may relate to temperature, chloride concentration, presence of moisture, oxygen concentration, redox potential, etc. The possible techniques that may be applied will depend upon the system under consideration i.e. fully immersed in the internal production environment or placed in the external insulation or on the surface of pipework.

Additional considerations arise in ensuring appropriate placement or, ensuring that the sensor location will truly capture the conditions that may lead to SCC. For example, where evaporation of water leads to salt cake formation on external surfaces, or the possible ultra-high concentration brines (“exotic brines”) which may be associated with internal SCC in very low oxygen concentrations; both potentially pose problems for in-situ field application.

2.2. ELECTROCHEMICAL CORROSION MEASUREMENT TECHNIQUES

The electrochemical potential is fundamentally related to the thermodynamics of corrosion reactions, while currents are related to the kinetics of corrosion. Electrochemical monitoring techniques include those which simply monitor a system without perturbation and others which impose perturbation and measure response of the system to determine the state of the metallic material. These can include measurement of corrosion potential, electrical resistance (ER), linear polarisation resistance (LPR), cyclic potentiodynamic polarisation, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN).

The principal techniques available for real-time monitoring of corrosion in stainless steel process pipework include direct electrochemical methods, such as electrical resistance and linear polarisation resistance (4-6). These techniques are widely used, however, ER and LPR techniques give poor correlation with localised corrosion, such as pitting and stress corrosion cracking, and are better suited to the measurement of general corrosion of materials such as carbon steels. Other methods monitor the corrosion damage using NDE techniques or indirectly assess the risk of corrosion by measuring the corrosivity (pH, chloride concentration, temperature, concentration of certain corrosive species, etc) of the process stream and correlating with supporting data on corrosion rate or environmental cracking susceptibility.

Electrochemical noise monitoring has been developed alongside the other techniques and it has been used in assessing both general corrosion and localised corrosion phenomena (7-11), and it is probably the best electrochemical method for detecting and monitoring localised corrosion such as pitting, crevice and SCC (4,11). EN constitutes the rapid monitoring of fluctuations of both/or either the free electrochemical potential and the electrochemical current in a freely corroding system (i.e. without externally applied current or voltage) resulting from the initiation and repassivation of metastable localised corrosion. This allows assessment by data manipulation of discrete events and avoids the averaging of signals that traditional potential monitoring relies upon. The possible advantages of electrochemical noise over traditional electrochemical monitoring techniques such as ER and LPR are the rapid, real-time response to system changes, the passive monitoring of the process stream corrosivity and the capability to detect and discern between different localised corrosion mechanisms.

Available data in the public domain pertain to laboratory scale EN trials on a limited number of materials, mainly 300-series austenitic stainless steels (12-16), and field experience in live plant is very limited (17-19). Environments reported included de-ionised water and a range of more aggressive media such as CO-CO_2-H_2O systems, boiling 42% $MgCl_2$ solution or aqueous solutions of $NaNO_2$, NaCl, HCl, H_2SO_4 and Na(SCN). EN characteristics such as electrochemical potential and/or current pulse, amplitude, shape, number of noise transients in a given time and their standard deviation have been used to distinguish SCC from other corrosion events and for monitoring of initiation of the SCC process in austenitic stainless steels. Monitoring of change in potential fluctuation (potential noise) in stressed specimens prepared from sensitised 304 stainless steel and immersed in a chloride solution at temperatures up to 80°C (14) showed that propagation of cracks was associated with higher amplitude in the potential fluctuation. In one study where slow strain rate tests were carried out in high purity-oxygenated water at 288°C and total pressure of 8.2MPa, corrosion current noise (pulses) from sensitised type 316 stainless steel showed that SCC conditions were associated with higher peak and slower decay rates than those from the non-sensitised specimens (15,16). It was suggested that electrochemical current noise measurement could provide real-time monitoring of SCC in austenitic stainless steels in high-temperature, high-pressure water. However, no data are available regarding EN monitoring on duplex stainless steels in laboratory or in actual plant.

Commercial implementation of real time EN monitoring in plant and field applications is at an early stage and, therefore, available information is limited. One commercial system has been claimed to be capable of real time monitoring of localised corrosion and SCC in a non-ferrous alloy (brass), steel and austenitic stainless steel plant (20,21) including a sour gas pipeline and an acetic acid pilot plant. The technique employs electrodes that are manufactured from the same material as the process equipment which are submerged in the process stream assuming that the electrodes will corrode in a manner similar to that of the structure. However, no reference was made specific to SCC monitoring of duplex stainless steels. Although in-house trials might have taken place on this material, discussion by TWI with third parties and experts in the field confirmed the lack of data for duplex stainless steels.

A drawback of the EN technique is that it assesses the corrosion behaviour of a structure based on data that are collected from specific location(s) and, therefore, corrosion events that may occur at other locations of the plant/structure will not be detected. Thus, behaviour elsewhere must be implied by extrapolation from the measurement locations. Inaccessible locations will typically therefore be problematic e.g. difficult to reach topside pipework, or subsea flowlines and pipeline installations.

A critical step in identifying whether EN of DSS is appropriate for a given application, is the demonstration and selection of an appropriate analysis strategy to discriminate between SCC and other corrosion events. The analysis technique needs to be customised to the particular application and type of structure. A number of data analysis techniques have been considered ranging from 'raw' data examinations to statistical analysis, chaos theory and wavelets analysis (11). Therefore, training key personnel, optimisation of the technique in laboratory and/or in pilot plants and signal calibration would be essential before the technique is successfully transferred to the field. Finally, handling a large amount of data (sampling frequencies are approximately 1Hz) requires robust on-site computing capabilities and data handling.

Other techniques such as ER, LPR, electrochemical impedance spectrometry and acoustic emission (6,11, 22-24) could be employed to complement EN monitoring to reveal both general corrosion and initiation of chloride SCC in hot environments. However, these techniques have been used mainly for the detection rather than monitoring of SCC for austenitic stainless steels on laboratory scale tests and no references are available pertaining to monitoring of chloride stress corrosion cracking in duplex stainless steels. Therefore consideration should be given to combining a range of techniques to ensure accurate indication of SCC without false calls. In this respect, data is required on the initiation time for SCC to occur under different conditions, and whether shorter durations may cumulatively lead to SCC.

It is noted that the above comments relate to immersed conditions suitable for internal assessment of process pipework. External SCC due to chlorides from the environment is difficult to measure due to the development of relatively localised areas with an accumulation of deposited salts due to evaporation of the majority of the water. For electrochemical measurements in situ this poses a significant problem. However, consideration should be given to the utilisation of probes fitted with a means of retaining salt on the surface whilst allowing water permeation to assess the salt cake or saturated solution influence on the material. This would allow testing of behaviour in these conditions within a bypass line for example, rather than attempting to predict formation within the plant and placing the probe in the same location. For example, a reverse-osmosis type membrane may allow water diffusion but prevent chloride migration away from the probe, thus offering a method of establishing system response. The behaviour in the bypass loop would then be extrapolated to the facility based on process knowledge.

2.3. ENVIRONMENTAL MONITORING

In cases where the SCC controlling parameters are well understood and the envelope for safe conditions has been established, then it is theoretically possible to consider a monitoring approach based on the on-line measurement of the variables, assuming that the material is inherently susceptible to SCC. For example, at welds, it is generally assumed that the residual stresses will approach the yield value and therefore, monitoring of temperature, oxygen concentration and chloride may allow prediction of whether the environment is capable of inducing SCC. Such measurements would need to be taken on-line to ensure that system upsets are captured, but the system must not lead to false calls.

This approach also requires knowledge of initiation periods for SCC and variation across the SCC envelope and whether cumulative effects need consideration for conditions which are in themselves deemed safe. Laboratory studies would be required combined with trials on full-scale pipe work etc for industry to gain confidence in such an approach. Replication of all the fabrication variables present in a typical plant would be a significant challenge in such an exercise.

3. CONCLUSIONS

3.1. INTERNAL SCC

1. There are no laboratory or industrially proven solutions for electrochemical monitoring of internal stress corrosion cracking in duplex stainless steels, but several technologies have been the subject of promising laboratory trials for other materials.

2. The principal techniques available for real-time monitoring of internal corrosion in stainless steel process pipework, i.e. electrical resistance and linear polarisation resistance, give poor correlation with localised corrosion and are not suitable to monitor chloride stress corrosion cracking alone.

3. Electrochemical noise monitoring has been used in assessing both general corrosion and localised corrosion phenomena in laboratory and plant for a range of materials. Whilst data specific to duplex stainless steel are not available, it is probably the best candidate direct electrochemical method for detecting and monitoring localised corrosion in stainless steels.

4. In cases where the SCC controlling parameters are well understood and the envelope for safe conditions has been established, then a monitoring approach could be considered, based on the on-line measurement of the process variables, assuming that the material is inherently susceptible to SCC.

5. It is possible that one technique in isolation may be capable of monitoring SCC in duplex stainless steels, but it is more likely that a combined electrochemical/environment/non-destructive evaluation strategy will be required to mitigate the risk of failure.

3.2. EXTERNAL SCC

6. There are no laboratory or industrially proven solutions for electrochemical monitoring of external stress corrosion cracking.

7. There are many practical difficulties in electrochemical monitoring external SCC, but use of a modified probe, fitted with a means of retaining salt on the surface whilst allowing water permeation, may allow the assessment of salt cake or saturated solution conditions.

8. Given the practical difficulties associated with electrochemical methods as applied to external SCC, then a monitoring approach should be developed, based on the on-line measurement of critical variables, assuming that the material is inherently susceptible to SCC. Measurement locations could be modified to replicate worst-case conditions for inaccessible locations on site.

4. RECOMMENDATIONS

Given the safety advantages of pre-empting the on-set of SCC, as opposed to post-crack detection, it is recommended that the most promising techniques identified in the present work be developed further and that guidelines be produced for their industrial application. It is recommended that the following items be addressed by industry:

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- Definition is required of industrially relevant environmental parameter envelopes in which the likelihood of SCC of welded duplex stainless steels is significant. This should be established by review of existing data and experience, and specific laboratory testing.
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- Appropriate long-life probes, including the incorporation of stressed specimens, should be assessed/developed.

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- The use of in-situ monitoring needs to be incorporated into a risk based inspection strategy, incorporating appropriate NDE as a response to any indication that the likelihood of SCC has risen above a critical level.
- Ultimately, for plant processes that necessarily operate in regimes known to present a significant threat of stress corrosion cracking to duplex stainless steels, serious consideration should be given to means of providing surface protection or even use of alternative materials in high risk areas.

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