Performance of Duplex Stainless Steels in Hydrogen Sulphide-Containing Environments

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Abstract

This paper addresses relevant past papers in previous 'Duplex' conferences in the light of present-day knowledge, and shows which aspects have been emphasised at different times over the last 15 years. From this review conclusions are drawn which may assist in making decisions on the application of duplex stainless steels in future. A critique of currently used and mis-used test methods is included.

Keywords

SSC review test-methods fit-for-purpose H_2S

1. Introduction

In the current climate of selecting materials which are strictly fit-for-purpose and without any over-design, duplex stainless steels represent a potentially cost-effective option for use in oil and gas production systems. In order to exploit them to their full requires a good level of understanding of the possible failure mechanisms which may arise in the different environments and good characterisation of the materials response. This becomes increasingly important as fields for exploitation tend to more aggressive (high pressure and temperature) conditions.

The key issue is the conditions under which duplex stainless steel may be applied focusing upon the environmental limitations.

First it is necessary to define the potential corrosion risks:
- generalised corrosion
- localised corrosion
- hydrogen embrittlement
- sulphide stress corrosion cracking

This paper is concerned with the last of these as this is often the limiting factor in application of duplex stainless steels in H_2S-containing oil- and gas-field applications.

Various factors affect the evaluation of field performance:

1). Material Factors

It is necessary to be clear which type of steel is being discussed since it has long been recognised that there are various "families of duplex stainless steels" distinguished by composition:

- low alloy e.g. UNS S32304
- 22Cr e.g. UNS S31803, UNS S32205
- 25Cr e.g. UNS S32550
- super duplex, 25Cr e.g. UNS S32750, S32760

The condition of the material (e.g. the level of cold work, presence of welds) is also critical to the performance in service.

2). Environmental Factors

It has long been recognised that the duplex stainless steels are limited in the level of H_2S and temperature to which they can be used. It is now well accepted that the materials are sensitive to specific levels of chloride ion content and also pH. It is also evident that in field environments the presence of hydrocarbons has a beneficial effect upon the performance of materials. The choice of relevant test environment when carrying out laboratory evaluation of performance should be made with care and environmental control is critical, particularly the avoidance of oxygen ingress.

3). Test Method Factors

The choice of test method and sample configuration selected will affect the likelihood of failure in the tests and therefore the conclusions reached. This could lead to the rejection of material for a purpose for which it might be perfectly acceptable. This means that care should be taken to select test geometries and methods which are pertinent to the application in question[1].

The acceptance criteria will affect the conclusions reached in any particular set of tests. Most of these points have been addressed in detail in publication EFC17[2].

The literature on the performance of duplex stainless steels in H_2S- containing environments is already extensive. For example, a review of more than 200 papers on this topic has been made by TWI as part of a larger piece of work on behalf of a group of sponsors[3,4]. For this paper it was felt to be pertinent to address at least the majority of the relevant past papers in previous 'Duplex' conferences in the light of present-day knowledge, and to show which aspects have been emphasised at different times over the last 15 years. From this review conclusions are drawn which may assist in making decisions on the application of duplex stainless steels in future.

2. Literature Review

At the first 'Duplex' conference in 1982 in St. Louis, Missouri, one full session of 9 papers was dedicated to duplex stainless steels in sour gas well applications. Thus the emphasis was on the performance of the alloys, particularly when cold-worked (as for downhole grades) and in the absence of weldments. Several of the papers refer to alloy development and composition optimisation which has subsequently resulted in the establishment of commercial grades of steels.

Onoyama et al[5] carried out sulphide stress corrosion cracking (SSC) tests on materials of various compositions with 0.5% proof strengths in the range of 568-915 MPa. The test conditions may be regarded as fairly severe (NACE solution at 80°C) but it is important to note that the key aim of this work was parameter testing to establish an optimum composition from the various alloys investigated and therefore it was necessary to obtain failures in tests within reasonable periods of time (around 100 hour testing was utilised). The paper illustrates how the optimum composition was derived by considering the beneficial effects of N, Mo and Ni additions and the harmful influence of Si and higher amounts of Sn and Sb.

The paper then goes on to consider the properties of the optimised composition duplex stainless steel (25Cr -7Ni- 3Mo -0.5Si -0.5Mn -0.15N -0.05Sn) utilising spring loaded tension test specimens (diameter 3mm) and slow strain rate specimens tested at $3x10^{-6}$/s. Tensile test specimens stressed up to 120%YS did not fracture after a test duration of up to 500 hours in the NACE solution at 35°C. Further testing of spring loaded tensile specimens in the NACE solution at 80°C did result in failures at high stress levels. Dissolution of the austenite grains giving pitting followed by cracking through the ferrite grains was stated to be the mode of failure (whilst other references have noted preferential attack of the ferrite phase). The results indicate that at very low concentration of NaCl the material can tolerate quite high levels of hydrogen sulphide (at 0.5g/l NaCl, 0.5% Acetic acid, 80°C and 1bar H_2S there was no reduction in tensile strength ratio in slow strain rate testing whereas at higher levels of NaCl (50g/l) cracking was experienced in tests with more than 0.1bar H_2S). Increasing the chloride content raised the cracking susceptibility, although above about 5g/l NaCl there was no apparent worsening of performance. Increasing the H_2S partial pressure significantly increased the SSC susceptibility with even a small amount, 0.01bar, giving some reduction in crack resistance compared to completely sweet conditions. A clear maximum susceptibility to cracking was noted at 80°C. The paper comments on the applicability of the test results to service and notes that test specimens were fully immersed in the aqueous solution while in practice exposure would be only on the inner wall of a tubing. Also, in service, a certain amount of hydrocarbon might be present which may inhibit corrosion.

Later work has indicated a more pronounced influence of chloride levels above 5g/l NaCl than this early work although direct comparison is not possible as the test conditions are not identical[6].

Since this time considerable work has been carried out at the National Physical Laboratory (NPL) over several years on the diffusion rate of hydrogen in duplex stainless steels[7]. It has been shown that diffusion rates are, in fact, very low, such that it might take more than 70 days to achieve 65% of the steady state hydrogen concentration at a depth of 500µm in 22Cr duplex stainless steel at 80°C. These data have a number of implications in the context of corrosion test duration. It is important to consider the mechanism of cracking in this context too. In the case of SSC in duplex stainless steels, cracks are generated from the surface and therefore the bulk hydrogen content is less critical than in corrosion mechanisms where cracks are generated subsurface (e.g. step-wise cracking in C-Mn steels). The propagation of a surface generated crack in a corrosive environment itself generates hydrogen in rupturing the surface film. Thus, hydrogen is present at the crack tip in the critical plastically deformed zone. In the case of a SSR test cracks form at the surface and, when tested in the corrosive solution, hydrogen forms at the crack tip and will influence the strain to failure in materials which are sensitive to hydrogen embrittlement effects. Such effects will be evident even though the diffusion of bulk hydrogen from the surface may lag significantly behind the crack tip itself. Bulk hydrogen *can* influence test results, for instance it has been shown that a specimen pre-saturated with hydrogen in a corrosive environment will show SSC when tested in air[8]. In this case hydrogen already present in the metal is diffusing rapidly to the plastic zone at the crack tip. Further discussion of the effect of hydrogen on the cracking mechanism is provided by Verneau et al[9]

For constant strain tests pit initiation may be the critical step in initiating a crack and, if that crack is to propagate, then the bulk metal needs to be hydrogen saturated. Thus, for such tests, time is a much more critical variable. If a test duration is 30 days but two or three times this period is needed to build up the equilibrium hydrogen profile then no hydrogen embrittlement effects or crack propagation may be observed whilst they could happen in practice. A number of cases have been reported where cracking was not observed in 30 day tests but was noted after 60-90 days[10,11]. It has been postulated[10] that there is a change in the nature of the surface film from oxide to sulphide at higher temperatures (@200°C) correlating with a transition from pitting attack to general corrosion. This also impacts on the test duration. If the medium is aggressive then there is rapid initiation of pits so then short term testing is suitable. In more marginally aggressive environments longer term testing is required for pit initiation.

The observation that it takes a long time for hydrogen to diffuse into duplex stainless steels also suggests that there is *less* fundamental difference between a small scale specimen exposed on all sides and the real world where exposure is only on one side. It cannot be argued that the small specimen is unrealistically highly-charged with hydrogen relative to the field situation.

The beneficial contribution of an oil phase to corrosion reduction in corrosive oil wells mentioned by Onoyama and in other references has been commented on by several workers in the context of carbon and low alloy steels but rather few have attempted to quantify the effect for corrosion resistant alloys. Galindez Ruiz and Craig[12] investigated corrosion rates and also cracking of various alloys including 22Cr duplex stainless steel in the following conditions:

- 143°C, 0.34bar H_2S, 47.9bar CO_2 (total pressure 48.2bar) and in an emulsion of 20% water in oil.

No cracking was observed in the 22% Cr duplex stainless steel tested using C-rings stressed to 80% of actual yield strength according to NACE standard TM0177. Corrosion tests in the same conditions with 100% water indicated rather high corrosion rates which were reduced by a factor of 8 in the presence of 80% oil under these conditions. The implication of this work is that higher concentrations of H_2S may be tolerated in the presence of an oil emulsion compared to wet gas whilst precise limits cannot be deduced on the basis of this limited information.

Also in 1982, Sakai et al[13] gave details of tests carried out to optimise the composition of alloy NKCr22 (22Cr-5.5Ni). The performance of that material in H_2S-Cl environments was tested using SSRT equipment at an extension rate of 1.2 x 10^{-6}/s. The test environment contained 20% NaCl, 25bar CO_2 and various low levels of H_2S. The temperatures investigated ranged from 25°C to 200°C. The conclusion was that there was a lower limit of H_2S of only about 0.02bar above which there was a risk of cracking at temperatures below 140°C. Above that temperature the material could tolerate much higher levels of H_2S (0.1bar at 150°C and probably 1bar or more at 200°C).

Although the pH of these tests is not quoted it may be estimated using Annex C of publication EFC16[14] as being at about 3.5 depending on temperature assuming that no buffers were added to the solution. Even considering this fairly low pH value the limiting H_2S partial pressure given by this work is extremely low, reflecting the severity of testing.

A much lower apparent susceptibility to cracking is indicated in a paper on the performance of Ferralium alloy 255[15]. This paper indicates no cracking in C-ring specimens stressed to 90-95%YS at 0.06bar H_2S in temperatures from 25-232°C in CO_2/H_2S/Cl environments (chloride content 25% NaCl). The paper states that much emphasis is placed on ambient temperature data particularly for acceptance into NACE standard MR0175 and a table of test results conducted to TM0177 (1bar H_2S) are presented in support of the acceptance of this material into NACE MR0175. With the exception of materials in a non-optimum heat treatment condition the results are generally very good when stressed at up to 92% yield. On the basis of this information the solution annealed alloy was included in MR0175 by 1984 without any stated limitations of exposure to H_2S.

Further tests quoted in the paper were carried out at 149°C with only 0.1bar H_2S and these showed cracking in the presence of 25% NaCl and 90% CO_2. This is a very clear illustration of the fact that, if the wrong test is used for the admission of a material to NACE Standard MR0175, and it is misinterpreted as implying the material is suitable for service in *any* sour environment, failures could readily occur if the temperatures got as high as 149°C (or, indeed, around 80°C). Evidently, room temperature testing is not applicable for evaluating performance over a wider temperature ranges in a material which shows maximum susceptibility to cracking at more elevated temperature conditions. This point has become more widely recognised by the committee responsible for MR0175 over the last 15 years and increasingly detailed descriptions of environmental limitations are now included as newer alloys are added to this complex document, with the ironic result that many *better* materials developed in recent years are more restricted in application than older materials. This point has been recently very well presented by Francis et al[16] who advocate fitness-for-purpose testing and suggest that where duplex stainless steels are thought likely to be a useful material but the environmental conditions are outside the scope of MR0175, testing as specified in publication EFC 17[2] should be carried out.

If we compare the results obtained in these two papers there is a large difference apparent in the cracking susceptibility of the materials. Whilst some improvement in cracking resistance would be expected in the case of 25Cr duplex stainless steel (Ferralium 255) relative to a 22Cr duplex stainless steel, undoubtedly there is also some influence of the test method. Tensile specimens (as used in the SSRT work by Sakai et al[13]) are less representative of the material to be used in service than the C-rings utilised by Kolts since the material is taken from the mid-thickness of the steel rather than the surface. The direction of stresses in tensile samples is also perpendicular to that in C-ring specimens.

For deep sour wells not only does the pressure and temperature increase but often super-saturated chloride contents are found. Vallourec[17] investigated the performance of duplex steel VS22 in sodium chloride contents of 100g/l. Tests were made using U-bend and C-ring specimens in an autoclave at temperatures from 130°C to 230°C. The data presented indicate that the partial pressure of H_2S under such conditions should be *less than* 0.3bar to avoid sulphide stress corrosion cracking since cracking was found under these test conditions. Insufficient data are presented at this stage to determine environmental limits for the material.

A compilation of SCC test data and practical experience but was made by Bernhardsson for Sandvik Alloy 3RE60[18]. This compilation indicates a risk of failure in applications above about 150°C except in chloride contents below 10ppm when higher temperatures can be tolerated. The paper does not quote sufficient information on either the pH or the H_2S content to allow any conclusions to be drawn on these limits on performance and this data has been largely superseded and more recently developed grades would be expected to show superior properties.

In 1982 the amount of data available for alloy SAF2205 was much more limited than for 3RE60 but preliminary corrosion test results were presented[19]. Longitudinal tensile specimens were tested in water containing 5 or 15% NaCl with a partial pressure of about 70bar of CO_2 with mixtures of H_2S and methane to make a total system pressure of 100bar. Constant load testing up to at least the yield strength on cold worked SAF2205 tubing showed a limiting partial pressure of H_2S of about 0.1bar up to 150°C above which higher levels of H_2S could be tolerated (e.g. about 1bar above 200°C). The pH in these tests is estimated[14] at about 3.

This paper also included some interesting tests at two pH values i.e. 3.9 and 2.5 (0.5% HAc). The threshold limit for cracking at the higher pH was just below 1bar of H_2S even at 100°C whereas at low pH the threshold was estimated at 0.05bar H_2S, clearly illustrating the beneficial effect of higher pH on cracking performance which is now so widely recognised. These tests were longitudinal tensile specimens tested at atmospheric pressure. It may be estimated from the data presented that at pH3 and 150°C the limiting partial pressure of H_2S would be about 0.1bar. This is consistent with the high pressure testing, indicating that total pressure is not a significant variable in testing duplex stainless steels. Comparison of the test results at 1bar and 100bar is valid since the test method is identical in both cases.

Later studies of the effect of pH have been made which show the same trend of decreasing H_2S limit with decreasing pH whilst the precise numerical relationship between these variables is different[20].

CAPCIS have undertaken several sets of work at elevated pressure (300bar), investigating the cracking resistance of 22Cr duplex stainless steel welds and weld repairs. For weld testing the preferred specimen type is 4-pt bend and in this case the samples were loaded to 72% of the 0.2% proof strength (stress level based on the design code). The environment contained 24bar CO_2, 0.05bar H_2S (estimated[14] pH of 3.2) and 63.5g/l chloride ion. After exposure for 720 hours at 90°C all specimens were found to be free of cracks. Whilst these conditions are not very severe this level of H_2S is 2.5 times the limit quoted for this grade of material in NACE MR0175.

High pressure testing was also reported by Kopliku et al[21]. Welds in 22Cr duplex stainless steel were tested in 45bar CO_2, 0.05bar H_2S (estimated[14] pH of 3.2) and 95g/l NaCl at a total pressure of 180bar made up with nitrogen. Four point bend specimens (some pre-strained by 3% to simulate the effects of reel barge laying) were tested at 72% and 95% of the specified minimum yield strength at 100°C for 720 hours. No cracking was detected.

The influence of coupling of duplex stainless steels to carbon steel is briefly commented on by Craig[22] and in more detail by Mukai[23]. It was noted by Mukai that coupling of samples of duplex alloy DP3 to carbon steel decreased the threshold stress to about 70% of the yield strength suggesting that cracking is due to hydrogen embrittlement in the NACE solution at room temperature. Uncoupled samples did not fail in NACE TM0177 tests. Tests were made on annealed and cold worked (P110 grade) alloy DP3. Maximum susceptibility to selected dissolution of the ferrite phase was noted at around 80°C although the corrosion rates were very low. The susceptibility to SSC was determined at 30bar of CO_2 and chloride content ranging from 5%-25%. Various test specimens are discussed in the paper 3- and 4-pt bend specimens with and without stress concentrating notches and C-ring tests as well as uniaxial constant load SSC testing. Interpretation of the information presented is difficult as it is not clear exactly which specimens have been used for the different tests. The implications of the test results at 5%NaCl and temperatures around 50-100°C are that there is a critical limit for cracking in terms of partial pressure of the H_2S of around 0.1bar but this increases slightly as the temperature rises to 200°C. However, at 25% NaCl, there is a slightly higher susceptibility to cracking so that even at 200°C the limiting partial pressure of H_2S is below 0.1bar. Annealed material was much more resistant to cracking and, at this time, it was estimated to be acceptable at up to 1bar H_2S in 5% NaCl at temperatures below 200°C (although longer term confirmation was to be carried out).

Rhodes[24] of Shell Development Company carried out extensive testing using C-ring samples, DCB and slow strain rate testing over a range of conditions. The results concur with those of other workers indicating a maximum susceptibility to sulphide stress corrosion cracking at around 80°C and this is explained in terms of a synergism of cracking influences including pitting corrosion and hydrogen embrittlement effects. Interestingly a direct comparison is made of different test methods under identical conditions (5.1M Cl-/CH_4-CO_2-H_2S at 177°C with about 0.2bar H_2S). C-rings compressed to the yield point did not show any SCC but failures occurred on notch C-rings, DCB samples and on slow strain rate test samples. In slow strain rate tests, cracking was indicated at partial pressures as low as 0.04bar at 177°C and even trace levels of H_2S were shown to have some impact on test results by introducing very low levels of pitting.

It is significant that already in 1982 Rhodes concludes that occurrence of SCC in any particular test medium was found to be sensitive to the test technique. In particular, specimen orientation, notch effects and dynamic straining are important variables influencing SCC initiation in marginal environments (high temperature or low H_2S). The results presented in this paper may be understood when it is appreciated that there is a fundamental difference between C-rings which are crack initiation tests and notched C-rings and DCB samples which are crack arrest tests. Slow strain rate tests are a combination of *forced* cracked initiation and crack growth tests which nearly always produce some effects with duplex stainless steels. It has been commented that a failure in an SSR test cannot constitute the failure of a material but should indicate that further investigation of its' properties and performance is necessary utilising alternative test techniques[25].

Considering the papers from the Duplex '86 Conference, there was a much lower emphasis on corrosion aspects. Guntz[26] tested 22Cr duplex stainless steels using 'U' bend, C-ring and 4-pt bend beam test in 100g/l NaCl, 50bar CO_2 and a 0.3 and 3bar H_2S. Temperatures ranged from 80-230°C and the pH is estimated[14] at 3.1. In all cases no cracks were observed after 21 days at stress levels of 90%YS. Developments in understanding of the mechanism of cracking and of test methods have lead to the proposal that constant strain tests should be made at 100% of the *actual* 0.2% proof stress of the material if potential cracking problems are to be detected[2]. Thus the absence of cracking in these tests may simply be an artefact of the test method. NACE TM0177 tests did not fail at up to 100%YS but the high resistance of the duplex stainless steels to cracking at room temperature is well established and, as indicated above, is no guarantee of good performance at elevated temperatures.

'U' bend specimens were also made on *welds* in this material under similar environmental conditions. In this case cracks were found at 130°C and 180°C at 3bar H_2S but no cracks were observed at 0.3bar H_2S. 'U' bends are useful only as a sorting test, the stress levels are so high and the edge effects so intense that any data should be viewed with caution. This type of specimen is now not recommended for evaluation of SSC resistance (ref.2 section 7.4).

The well established sensitivity of duplex stainless steels to cracking in the temperature range 60-90°C has been demonstrated by many different workers including Audouard et al[27] and Schofield and Kane[28]. Many workers have also shown the detrimental influence of cold work on sulphide stress cracking resistance particularly at ambient temperatures[29]. As the temperature approaches the critical range the difference in performance of cold worked tubulars and annealed tubing becomes much less marked as all of them show a deterioration in cracking resistance. Later, Barteri, et al[30] carried out a study utilising constant load, constant strain and SSR testing at a strain rate of 2.2×10^{-7}/s to establish an engineering diagram of safe use limits for duplex stainless steels. This work particularly highlighted the difference between annealed and grades cold worked up to a 140ksi yield strength. They concluded that the sour service limits could be defined as follows:

22Cr: 0.07bar - reduced to 0.015bar for grade 140
25Cr: 0.15bar - reduced to 0.025bar for grade 140
25CrW: 0.12bar for grade 140.

A very comprehensive study of the influence of chloride content and hydrogen sulphide content on the performance of 22Cr and 25Cr duplex stainless steels was carried out by Tsuge et al[31]. All the testing was fairly severe using slow strain rate testing at a strain rate of 4.2×10^{-6}/s and small size specimens with cross sectional area 2 x 2mm gauge section or 3mm diameter. All testing was carried out at 80°C. Figure 1, taken from this paper, brings all the results together in a convenient format allowing approximate thresholds of chloride content and H_2S to be established although, unfortunately, it is not clear whether these environments also included CO_2 and the pH is not quoted.

The sensitivity of 22Cr, 25Cr and Super 25Cr duplex stainless steel to temperature cycling between 80°C and 110°C has been investigated by CAPCIS in an environment containing 250g/l NaCl with 1psi (0.07 bar) H_2S. The test environment was made up to around 7bar with CO_2 and contained 1 x10^{-3} mol/l $NaHCO_3$ giving an estimated[14] pH of 3.4. C-ring samples tested at 100% of their actual yield strength (measured by strain gauging the inner surface) experienced daily temperature cycles for 33 days but no cracks were noted.

Given the combination of critical temperature range, high chloride level and high stress, failures might have been expected in the 22Cr duplex stainless steel, based on data such as that presented in Figure 1, although the pH_2S is too low to be expected to give any cracking in the more highly alloyed materials tested. The lack of failure is attributed to the more realistic test configuration of the C-rings versus the SSR tests, plus some possible difference in environment pH.

By 1991 there was a huge body of data available on the testing of duplex stainless steel in 'sour service' conditions. A key question in considering how to compare all the various data generated by different laboratories is the different practices used for carrying out stress corrosion cracking tests. This subject was discussed in a review of various test methods made by Schofield, et al[32]. This paper draws attention to the fact that there was insufficient data on field experience in the literature at this time to clearly correlate one particular type of test as being the optimum for predicting field service performance. The same concern may still be legitimately expressed today - a detailed review of successful field applications of duplex stainless steels is certainly needed.

Slow strain rate testing was felt, by Schofield, to be useful in that it is rapid and it gives information on the cracking mechanism. Also, it is relatively easy to run extra tests and can be used for quality control purposes. The slow strain rate test was stated, however, to be controversial in that it is possible to get false test results where apparent failures may be observed at very low levels of H_2S, even as low as 4ppm, and incorrect interpretation of the fracture surface can give rise to false passes (if the fracture appears ductile). The paper argues the case that, on the whole, SSR testing is quite appropriate and that anomalies between results obtain by SSR testing and other test methods or service experience may be explained by consideration of an inappropriately selected strain rate. In some cases there is also the possibility of an incorrect electrochemical potential having been adopted because the specimen is not electrically isolated from the test apparatus etc.

A draft test specification for SSRT has been submitted to the NACE TM0177 committee and it is expected to be approved shortly. A round robin test series was conducted, with alarmingly variable results, hence the delay in its' approval.

The use of SSRT samples for investigating the behaviour of welds is inappropriate as it only effectively tests the bulk weld filler metal rather than the weld root (which may be made with a different consumable) and also the sample does not preserve the weld geometry.

An attempt was made in the paper to establish cases where various different test methods have shown good correlation, however, there were an equal number of examples where the correlation between different test approaches was rather poor. The key element that the authors establish is that if plastic straining is necessary to induce stress corrosion cracking and it is assumed that this may arise in service (which in these days is not really disputed) then it is necessary that the test should involve some element of plastic straining.

In this context it is worth noting that the elastic limit of duplex stainless steel is about 60% of the 0.2% proof stress, therefore, even any constant load testing undertaken above this level will induce some plastic straining.

Schofield and Kane[28] compiled threshold pH_2S cracking values for 22Cr and 25Cr duplex stainless steels from a dozen references which neatly illustrate the lack of consensus on this issue. It is impossible to rationalise such a variety of results which cover different material grades, test techniques, environments etc. The argument for establishing a clear, *relevant*, test protocol, is very strong[2,16]. This paper, and another[33] also notes the influence of heat tints at welds in lowering a materials' resistance to pitting and cracking, illustrating the importance that the surface finish of samples may have on the results obtained in corrosion tests.

Unpublished work undertaken by CAPCIS has also shown the influence of surface finish[11]. Autoclave tests were run at 90°C in an environment containing 0.72bar H_2S, 55bar CO_2, 90g/l NaCl giving a calculated pH of 3.1. Both annealed (YS=588MPa) and cold worked (YS=951MPa) alloy 2205 material was tested. The samples were C-rings, internally loaded at up to 100%YS with 3 surface conditions:

- as-received
- machined and polished
- machined and polished with the addition of ball indents to simulate pilger marks

Pitting was generally observed in the as-received samples and in the base of the ball indents. The fully machined samples showed superior performance illustrating that erroneous conclusions might be reached if only these machined test specimens were considered. In 90day tests cracks were observed in cold worked samples but not in the annealed material.

Blanchard[34] shows that C-ring tests are more severe than 4-pt bend tests (where the samples have been taken longitudinally from the pipe). This can be explained by the nature of the stresses in the longitudinal direction in the latter case and transverse for the former one. This higher cracking resistance of duplex stainless steels in the longitudinal orientation has been demonstrated in several studies[29,30]. In the case of the 4-pt bend tests the stress is also parallel to the direction of grain orientation whereas it is perpendicular to the elongated grain structure in the case of C-rings and these would therefore be easier to crack. This illustrates that the microstructural anisotropy of duplex stainless steel needs to be considered carefully in selecting appropriate test methods.

The keynote paper on environmental cracking from the Duplex conference in 1994[35] illustrated that despite all the various concerns which are expressed, duplex and super duplex stainless steels do in fact have good resistance to sulphide stress corrosion cracking particularly at pH in excess of 4. Taking data from other surveys Francis shows (Figure 2) that there is a strong dependence of SSC resistance on chloride content at high chloride levels (above 100,000mg/l) and on H_2S content at low chloride levels. These data are for pH values below 4. At higher pH levels the preliminary data indicated at this time that super duplex stainless steels such as Zeron 100 were resistant to cracking up to at least 0.7bar H_2S. The paper also commented that there are a few examples of duplex stainless steels in service at conditions more aggressive than these various limits. The successful applications might be because of the beneficial influence of the service environment pH values or the influence of hydrocarbons in the environment. Alternatively, they could simply be a reflection of conservatism in the type of testing carried out.

The design conditions for some field applications of a 25Cr super duplex stainless steel are listed by Schofield[36]. The table of data is repeated below with the pH estimated from ref.14 also given.

Table 1 Some design conditions for 25Cr superduplex stainless steel

Field	**Temperature**	**Chloride ion**	**CO_2 (bar)**	**H_2S (bar)**	**EFC16 (estimated) pH**

	(°C)	(ppm)			
Vesslefrik	110	10,000	6	0.01	3.7
Piper Bravo	98	25,000	8	0.06	3.6
Saltire	98	31,000	7	0.05	3.6
Embla	150	50,000	50	0.07	3.3
East Brae	115	30,000	25	0.20	3.4
Scott	135	80,000	2.1	0.02	4.0
Pelican	108		23	0.02	3.4
Nelson	104	20,000	7.5	0.06	3.6
Arco	107	16,000	10	0.14	3.6
West Sole	102	25,000	7	0.07	3.6
	103	30,000	3	0.10	3.8

These data are generally within the limits of failure data from many laboratories (e.g. Figures 1 and 2), but should not be interpreted as the definitive limits of field application. Testing of specific alloys, in the actual condition they will be applied in the field, in yet more severe environments than these might still demonstrate quite acceptable performance.

Rather few tests have been reported in flowing conditions but Barteri[37] has indicated that flowing tests are less aggressive than laboratory autoclaves under identical environmental conditions. This is suggested to be due to the beneficial effect of the fluid flow in removing corrosion products from the surface and in limiting pit initiation thereby reducing the likelihood of stress corrosion crack initiation. Obviously, such factors might also play a role in real service environments.

3. Discussion

The selection of materials that is based on laboratory testing requires judicious selection of test method and extreme care with the interpretation of the results. It is important to have a very clear preconception of the following issues:

1. The relationship of the test specimen to the item in service. This requires selection of the correct type of material, be that wrought, cast, forged or in a welded condition.
2. The anticipated failure mechanism. For example, whether the environment will cause pitting, in which case the interest is in crack growth tests (notched specimens) or if pitting is not expected then smooth C-rings or 4-pt bends are appropriate.

The first point above also raises the issue of whether the surface profile is important, in which case the use of materials in the as-received condition are appropriate rather than specimens with a machined finish. The second point above implies that a logical sequence of testing would be to first carry out exposure tests to establish whether pitting is a matter of concern.

Over the last 15 years there has obviously been considerable work undertaken in investigating the cracking resistance of duplex stainless steel in H_2S-containing environments. Published data on duplex stainless steels can therefore be contradictory unless the reader has a good understanding of the mechanisms of crack initiation and growth, and the purpose of the testing.

The crack susceptibility has been widely recognised to be dependant upon many variables: partial pressure of H_2S, pH, chloride content, temperature, microstructure, surface finish and test method.

It is probable that the influence of the test method is greater than generally recognised, in particular there seems to be a general lack of recognition of the significance of crack initiation tests and crack arrest tests.

The specific criticism of the SSR test method when applied to duplex Stainless steels relates to the change in mechanical properties which is an inherent feature of the test. Duplex stainless steels have been noted to show highly non-homogeneous cold working during the SSR test because of the differences in work-hardening capability of the austenite and ferrite phases[38]. Whilst acknowledging certain benefits of SSR testing as indicated in reference 31 for initial screening of alloys, SSR testing is not felt to be appropriate for testing duplex stainless steels for fitness-for-service since such dramatic changes of mechanical properties will not be a feature of normal service.

Qualification of duplex stainless steels for application in specific service conditions can be adequately established using the approach described in document EFC17[2] utilising the recommended specimen geometries and preferred, primary, test methods, viz. constant strain samples at an applied stress level equal to the yield stress, or constant load samples at 90%YS.

4. Conclusions

- Duplex stainless steels have shown excellent resistance to cracking in service in corrosive environments containing H_2S
- The H_2S limit for Duplex Stainless steels is a complex function of alloy composition, pH, chloride content, water chemistry, temperature, etc.
- The presently established limits of application of these alloys reflect some conservatism in the execution of laboratory tests and the interpretation of the results
- Careful appraisal of test techniques should be made prior to embarking on any testing
- SSR testing should not be used for fitness-for-purpose testing of duplex stainless steels
- Application of these materials in more aggressive conditions might be supported by judicious selection of laboratory test regimes

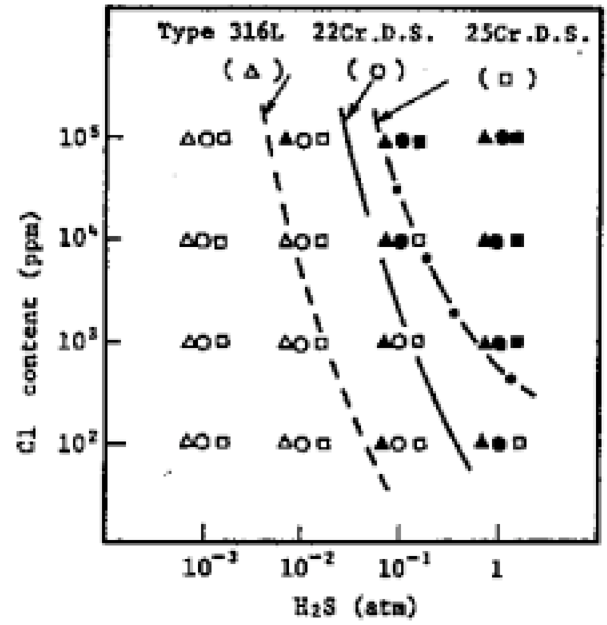

Figure 1. SCC susceptibility of 22Cr duplex stainless steel in Cl^--H_2S environment.
○ no SCC
● SCC

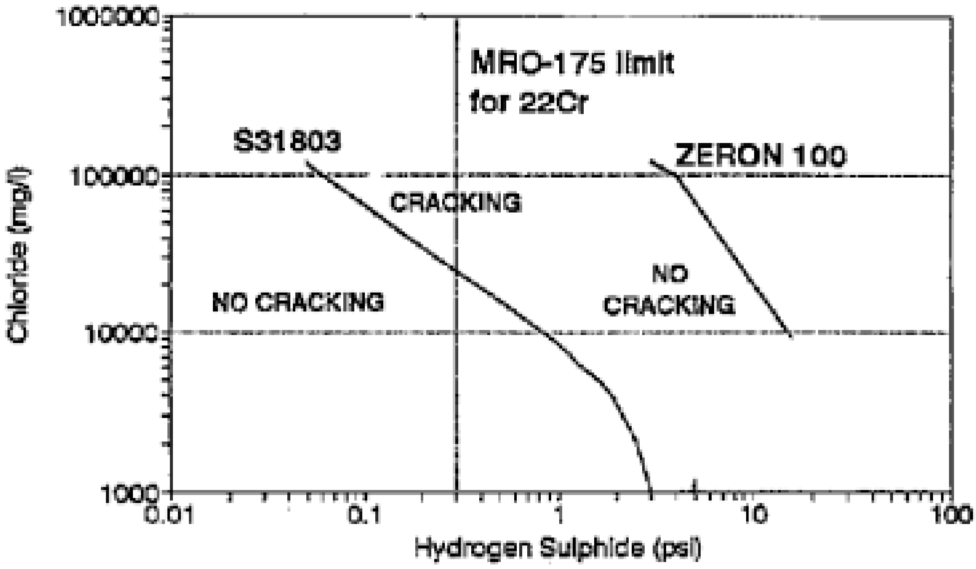

Figure 2. Suggested limits for duplex and super duplex stainless steels (pH<4).

References

[1] Clay, K. and Smith, L., "A Review of Corrosion test Methods for Sulphide Stress Cracking", Eurocorr '96, Nice, France 1996
[2] "Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for H_2S Service", EFC publication 17, 1996, Inst. of Materials
[3] Gooch, T.G. and Gunn, R.N., "Alloy Materials for Sour Service Environments - A Critical Review", TWI Report 5607/1/92, for a group of sponsors, June 1992
[4] Smith, L.S., "Alloy Materials for Sour Service Environments - CRASOUR2 an Update of CRASOUR",TWI Report 5681/1/96, for a group of sponsors, Nov. 1996
[5] Onoyama, M. et al, "Evaluation of Corrosion Resistance of a Duplex Stainless Steel in H_2S-CO_2-Chloride Environments", Paper 8201-009, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[6] Francis, R., "Environmental Cracking and Embrittlement of Duplex Stainless Steel", Paper KIV, Duplex '94 Glasgow, Scotland, November 1994, pub. TWI
[7] Turnbull, A. et al "Hydrogen Transport in Duplex Stainless Steels", Duplex'94, Glasgow, Scotland, November 1994, pub. TWI
[8] Private communication, Turnbull, A, NPL, June 1997.
[9] Verneau, M. et al, "Evaluation of the Corrosion resistance of Duplex Stainless Steels in H_2S and Chloride Containing Media", Eurocorr'96, Nice, 1996
[10] Schofield, M.J., "Electro-chemical Testing of Duplex Stainless Steel H_2S/CO_2/Chloride Systems", Duplex'94 Glasgow, Scotland, November 1994, pub. TWI
[11] Private communication, CAPCIS, unpublished work undertaken 1988
[12] Galindez Ruiz, NG and Craig, BD, "Effect of Crude Oil on Corrosion of Alloys in Severe Sour Environments", Materials Performance p.50, April 1995
[13] Sakai, J. et al, "Effects of Metallurgical Factors on Service Performance of Duplex Stainless Steel for Deep Sour Gas Well", Paper 8201-010, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[14] "Guidelines on Material Requirements for Carbon and Low Alloy Steels for H_2S-containing Environments in Oil and Gas Production" EFC publication 16, 1995, Inst. of Materials
[15] Kolts, J. "Properties of Ferralium Alloy 255 Duplex Austenitic - Ferritic Stainless Steel for Sour Gas Well Applications", Paper 8201-011, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[16] Francis, R. et al, "The Role of Environmental and Metallurgical Variables on the Resistance of Duplex Stainless Steels to Sulphide SCC", Corrosion '97, Paper 12, NACE.
[17] Prouheze, J.C., "Production of Tubing in Duplex Steel VS22 Influence of Cold Working on Mechanical Properties, Behaviour in Corrosive Sour Gas and Oil Environment", Paper 8201-012, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[18] Bernhardsson, S. et al., "The Stress Corrosion Cracking Resistance of Duplex Stainless Steels in Chloride Environments", Paper 8201-013, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[19] Tynell, M., "Applicability Range for a High Strength Duplex Stainless Steel in Deep Sour Oil and Gas Wells", Paper 8201-014, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[20] "Duplex Stainless Steels- Microstructure, Properties and Applications", Ed. R.N. Gunn, Pub. Abington Publishing 1997
[21] Kopliku, A, et al, "Corrosion resistance evaluation of 22Cr duplex stainless steel weldments", OMAE 1996, Florence, June 1996.
[22] Craig, B.D., "Evaluation and Application of Highly Alloyed Materials for Corrosive Oil Production", Paper 8201-015, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[23] Mukai, S., "Corrosion Behaviour of 25% Cr Duplex Stainless Steel in CO_2-H_2S-Cl Environments", Paper 8201-016, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[24] Rhodes, P.R. et al, " Stress Corrosion Cracking Susceptibility of Duplex Stainless Steels in Sour Gas Environments", Paper 8201-091, Duplex Stainless Steels 1982, St. Louis, USA, pub. ASM
[25] Discussion at EFC Working Party on Corrosion in the Oil and Gas Industry meeting
[26] Guntz, G., et al, "Austenitic-Ferritic Stainless Pipe For Acid Gas", Paper 12 Duplex '86 October 1986, NL, pub. NIL
[27] Audouard, J.P. et al, "Sulphide Stress Corrosion Cracking Resistance of Duplex Stainless Steel Plates", Duplex '86, NL, pub. NIL
[28] Schofield, M.J. and Kane, R.D., "Defining Safe Use Limits For Duplex Stainless Steels", Duplex Stainless Steels October '91, Beaune France, pub. Les Editions de Physique.
[29] Gustafsson, P. & Eriksson, H., "Duplex Stainless Steels in Chloride, CO_2 and H_2S Containing Media, Corrosion Properties", Paper 9, Duplex '86, pub. NIL, NL
[30] Barteri, M. et al, "Cold Working and Composition Effect on the Performance of Duplex Stainless Steels for OCTG", Duplex Stainless Steels October '91, Beaune France, pub. Les Editions de Pysique
[31] Tsuge, H. et al, "Corrosion Resistance of 22Cr Duplex Stainless Steel Chloride - H_2S Environment, paper 33b, Duplex '86, NL, pub. NIL

[32] Schofield, M. J. et al, “Applications Of Various Stress Corrosion Cracking Test Techniques: Validity and Relevance to Practice”, Duplex Stainless Steels October ‘91, Beaune France, pub. Les Editions de Physique.
[33] Kobayashi, Y. et al, Paper 52 Corrosion/88, NACE 1988
[34] Blanchard, F., “Duplex Stainless Steel Tubing and Casing for Sour Wells”, Duplex Stainless Steels October ‘91, Beaune France, pub. Les Editions de Physique.
[35] Francis, R., “Environmental Cracking and Embrittlement of Duplex Stainless Steel”, Paper KIV, Duplex ‘94 Glasgow, Scotland, November 1994, pub. TWI
[36] Schofield, M. J., “Electro-chemical Testing of Duplex Stainless Steel H_2S/CO_2/Chloride Systems”, Duplex’94 Glasgow, Scotland, November 1994, pub. TWI
[37] Barteri, M. et al, “Corrosion Test in a Flow Loop Simulating Sour Gas and Oil Well Environment”, UK Corrosion and Eurocorr November 1994, Bournemouth, pub. Inst.Materials.
[38] Abayarathna, D. and Kane, R., “Definition of Safe Service Use Limits for Use of Stainless Alloys in Petroleum Production”, Paper34, Corrosion ‘97, NACE 1997