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THE CORROSION OF DUPLEX STAINLESS STEELS IN SOUR SERVICE

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ABSTRACT

The high resistance to corrosion of 22 Cr, 25 Cr and super duplex stainless steels in chloride containing environments is well known. In sour service, resistance to stress corrosion cracking, pitting and crevice corrosion in the presence of CO_2 and H_2S is required. This paper presents the results of tests to determine the resistance of three duplex stainless steels to stress corrosion cracking, pitting and crevice corrosion at elevated temperature in a synthetic brine containing different concentrations of H_2S. The three alloys were UNS S31803, UNS S31200 (high Mo) and UNS S32760.

All three materials were tested in the cold worked condition, and loaded to about the 0.2% proof stress. The tests were conducted with 93 bar CO_2 and either 0.125, 0.25 or 0.375 bar H_2S. The results showed that only the super duplex alloy, UNS S32760, was resistant to SCC at 80°C at all of the H_2S concentrations. Pitting and crevice corrosion occurred at 121°C only at the highest H_2S concentration on all the alloys. The depth and severity of attack varied from alloy to alloy and indicated that super duplex UNS S32760 is more resistant than 25Cr, UNS S31200 (high Mo), which is more resistant than 22Cr UNS S31803.

1. INTRODUCTION

The resistance to pitting and crevice corrosion of duplex stainless steels in chloride containing environments is well known. Alloys with high chromium, molybdenum and nitrogen contents have the greatest resistance to corrosion, which can be broadly reflected by an empirical relationship known as the PREN number (PREN = %Cr + 3.3 x %Mo + 16 x %N_2). Downhole environments have chloride concentrations which commonly range from the 19,000 mg/l found in seawater to concentrations of 150,000 mg/l. In addition to chloride appreciable quantities of CO_2 and H_2S are usually also present. In this environment not only is resistance to pitting and crevice corrosion important, but also resistance to stress corrosion cracking (SCC). There is little published data on the performance of duplex stainless steels in sour process environments, and in particular there is little data comparing the commonly used grades of duplex and super duplex stainless alloys. To remedy this position, Weir Materials Limited co-ordinated a consortium of companies to fund a test programme to provide this data.

2. EXPERIMENTAL

Tests were conducted to assess the resistance of three duplex stainless steel alloys to stress corrosion cracking, pitting and crevice corrosion in a simulated process environment. The duplex grades were distinguished by their alloy content.

2.1 Materials

Three duplex alloys were tested, UNS S31803, UNS S31200, (high Mo) and UNS S32760. S31803 is a 22Cr duplex stainless steel commonly known as 2205. S31200 high Mo is a 25Cr duplex with a molybdenum content up to 3.0%. Alternatively, this alloy can be regarded as UNS S32550 without the copper addition. Alloy S32760 is a super duplex alloy marketed by Weir Materials Limited under the trade name ZERON 100. The chemical composition of the alloys are shown in Table_ 1.

The three alloys were supplied cold-worked to a minimum 0.2% proof stress of 758 MPa (110 ksi). In addition, S32760 was tested in the solution annealed condition. The measured mechanical properties and hardnesses are shown in Table_ 2.

2.2 Stress Corrosion Cracking

SCC tests were conducted in Hastelloy C-276 autoclaves. It is widely accepted that the resistance of duplex stainless steels to SCC passes through a minimum in the temperature range 80-100°C. Hence the present tests were conducted at 80°C.

Two C-rings and one 3-point bent beam specimen from each alloy were exposed in each autoclave. The C-rings were full wall thickness of the pipe with no machining except for cut ends. The rings were internally stressed using Hastelloy C-276 fasteners to about 100% of the specified minimum yield stress at room temperature, in accordance with the NACE T-1-F9 stressing equation. This was checked by the use of strain gauges. After the 30 day exposure the deflection of the C-rings was measured and no measurable reduction in deflection was observed. This indicated that no stress relief occurred during testing.

The 3-point bent beam specimens were prepared from the longitudinal direction of the pipe, at approximately mid-wall position. This was done to evaluate the stress corrosion resistance of these alloys when stressed in the longitudinal direction as would be the case when 'self weight forces' are experienced in a production string. The specimens measured 74 x 4.5 x 1.2mm and were of machined finish. They were stressed to 100% of the specified minimum yield stress of each material (room temperature properties), in accordance with the ASTM G39 stressing equation, in Hastelloy C-276 bending jigs.

After stressing, all specimens were placed in the relevant autoclave and the deaerated test solution was introduced. The test solution volume to surface area ratio employed was approximately 9 cm^3/cm^2. A CO_2/H_2S gas mix was bubbled through each autoclave for approximately 24 hours until measurements on the exit gas indicated that equilibrium conditions had been achieved, i.e. the exit gas composition was equal to the inlet gas composition. The autoclaves were heated to 80°C and the total pressure was adjusted to a nominal 93 bar.

The yield stress for these duplex stainless steels falls significantly with increasing temperature, resulting in a reduction of at least 10% between 20°C and 100°C. Thus the specimens could be considered to have been overstressed. However, actual yield strengths for the 22 Cr, 25 Cr and super duplex materials were 12.7, 10.3 and 16.8% respectively over the minimum specified. Hence the specimens were stressed to approximately 100% of the yield stress at temperature.

2.3 Pitting and Crevice Corrosion Tests

Two pitting corrosion coupons (in the form of stressed, bent beam specimens as described above) and one crevice corrosion coupon (25 x 20 x 1.1mm, drilled and fitted with two castellated glass-filled PTFE crevice formers) of each material were exposed in each of the three autoclaves at 121°C for 30 days. Excepting the test temperature, conditions in the three autoclaves were as described for the SCC tests in Section 2.2.

2.4 Test Environment

All tests were conducted in a synthetic brine similar to that which has been observed in some North Sea Fields. The composition is shown in Table 3. All tests were carried out at a total pressure of 93 bar which comprised CO_2 containing a small quantity of H_2S. Three H_2S concentrations were evaluated, designated as follows:-

low	H_2S	0.125 bar
mid	H_2S	0.25 bar
high	H_2S	0.375 bar

3. RESULTS

The test specimens were examined under a low power microscope, and microsections were prepared of interesting features.

The results from the stress corrosion cracking tests are shown in Table 4, from the pitting tests in Table 5 and the crevice corrosion tests in Table 6.

4. DISCUSSION

4.1 Visual Appearance

There was more black corrosion product on the corrosion test specimens than on the SCC samples. This is not surprising in view of the higher test temperature used in the pitting corrosion tests. There was also a difference in the appearance of the corrosion product with H_2S concentration at each temperature. At the low H_2S level, the black corrosion product was loose and poorly adherent. At the mid H_2S level, the scale was more adherent, while at the high H_2S level, the black product was thicker and very adherent.

4.2 Stress Corrosion Cracking

No cracking was observed on the bent beam specimens, but some of the C-rings in S31803 and S31200 showed cracks. It is possible that the difference in behaviour between the ring specimens and the beams is due to surface condition; it is frequently found that sulphide stress corrosion cracking initiates at sites of imperfections on a surface, e.g. bore-side machining marks, and the pipe material supplied for testing was of variable quality in this respect. A secondary testing factor which may have an influence is the possible difference in mechanical properties in the longitudinal (as tested by the bent beams) and transverse (as tested by the C-rings) directions. All cracks that were found were fine cracks and were associated with the edge of the C-rings. They were all in the position of maximum stress on the rings. Stressing was nominally to 100% of the room temperature yield strength. From a consideration of the reduction in yield strength at 80°C and the differing actual yield strength of the test materials, all the materials were stressed to about their actual yield strengths.

The loss of yield strength between 20 and 80°C is approximately 10% for cold worked material and 13% for annealed material and the actual stresses were: 22Cr(98% of actual yield strength); 25Cr, 101%; super duplex (cold worked), (95%); super duplex (annealed) 98%.

The cracks in the C-rings were typically as shown in Figures 1 and 2. The portions near the surface bear some resemblance to corrosion pits, with preferential phase dissolution evident along their entire length. All the cracks were located at the point of maximum stress on the C-rings. The cracks look somewhat of a cross between traditional fine intergranular/transgranular cracks and hemispherical pits. However, the attack on the C-rings was very different to the pitting in the stressed beams, shown in Figures 3 and 4.

The results from the C-rings show that alloy S31803 can suffer cracking at all the H_2S levels in the present tests. The S31200 (high Mo) alloy was more resistant to cracking, but cracking was observed at both the mid and high H_2S concentrations. S32760 showed no cracking at all three H_2S levels, in both the cold worked and solution annealed conditions.

The appearance of the attack on the SCC specimens indicates that the cracks originated from the base of corrosion pits. It seems likely that the more aggressive conditions found at the base of pits (i.e. low pH and high chloride concentrations) are required to initiate cracking. This, plus the fact that alloy S32760 showed no signs of pitting or cracking, suggests that the more resistant an alloy is to pitting, the more resistant it will be to sulphide stress cracking.

There is a wealth of data to show that the higher the chromium, molybdenum and nitrogen content of a duplex stainless steel, the higher is its resistance to pitting in aerated, chloride solutions, such as seawater. There is less data for process condition with high CO_2 and H_2S. However, work by Sandvik (1) has shown the beneficial effects of chromium and molybdenum on pitting resistance, while Tsuge (2) also found that 25 Cr duplex alloys had improved resistance to pitting compared with 22 Cr alloys. Finally Japanese work (3) has shown that high nitrogen containing alloys have superior pitting resistance in a sulphide containing environment. Hence there is evidence to support the conclusions of the present work that higher alloy content improves pitting resistance.

The PREN value (Cr% + 3.3 x %Mo + 16 x %N_2) is commonly used as an assessment of the resistance of an alloy to pitting in aerated chloride solutions (see Table 1). The present work suggests that it can also be used in process environments, not only as an indicator of pitting resistance, but also as an indicator of resistance to SCC.

4.3 Pitting/Crevice Corrosion

No detectable corrosion was observed on either the pitting or crevice corrosion specimens at both the low and mid H_2S concentrations. At the high H_2S level all three alloys suffered pitting and crevice corrosion to some degree. However, the results in both Tables 5 and 6 show that S32760 was more resistant to both pitting and crevice corrosion than S31803 and S31200. This is shown by the lower depth of attack in the pitting tests for S32760 and the fewer number of segments attacked in the crevice tests. The solution annealed S32760 showed no crevice attack, indicating a slightly superior resistance to crevice corrosion compared to cold worked material. Solution annealed material was not exposed in the pitting corrosion tests.

The morphology of the pits in alloys S31803 and S31200 high Mo is shown in Figures 3 and 4. They clearly show that preferential dissolution of the ferrite phase was prevalent.

5. CONCLUSIONS

The present tests indicate that there is a definite ranking order in resistance to SCC, pitting and crevice corrosion for the materials under test. S32760, super duplex, was superior to S31200 (high Mo), 25 Cr duplex, which was superior to UNS S31803, 22 Cr duplex stainless steel in the cold worked condition. This behaviour is consistent with the level of alloy additions in each material, the more highly alloyed being more corrosion resistant.

The results show that cracking originated from the base of the corrosion pits. This supports the view that in sour process environments the relative resistance to cracking can be indicated by the PREN value, previously used as a guide to pitting resistance.

No difference in the resistance to SCC of cold worked and solution annealed S32760 was discernible under the present test conditions as no cracking occurred. The solution annealed material appeared to be slightly more resistant to crevice corrosion than cold worked S32760.

ACKNOWLEDGEMENTS

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REFERENCES

1) P. Gustaffson et al - Duplex Stainless Steels '86, The Hague, Amsterdam, 1986

2) H. Tsuge et al - Metaux Corrosion Industrie No 667 1981, p337.

3) M. Onoyama - Duplex Stainless Steels Conference, Park, Ohio, USA, 1983

TABLE 1

Chemical Composition of Test Alloys

ALLOY	WT %											PREN
	Cr	Ni	Mo	N	W	Cu	C	Si	Mn	P	S	
UNS S31803	22.7	4.77	2.64	0.17	-	0.18	0.022	0.42	1.31	0.015	0.005	34.1
UNS S31200 (HIGH Mo)	24.6	6.52	3.15	0.195	-	0.21	0.03	0.63	0.76	0.020	0.006	38.1
UNS S32760 (COLD WORKED)	25.8	7.02	3.51	0.22	0.51	0.79	0.021	0.46	0.946	0.02	0.007	40.9
UNS S32760 (SOL ANNEALED)	25.1	6.9	3.52	0.21	0.65	0.59	0.021	0.30	0.60	0.023	0.005	40.1

TABLE 2

Mechanical Properties of Test Alloys (Room Temperature)

ALLOY	0.2% PROOF STRESS (MPa)	UTS (MPa)	ELONGATION (%)	HARDNESS (HRC)
UNS S31803	855	931	25.5	32
UNS S31200 (HIGH Mo)	836	985	19.2	31
UNS S32760 (COLD WORKED)	886	1013	14.7	35
UNS S32760 (SOL ANNEALED)	646	889	27	23

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TABLE 3

Composition of Test Brine

$CaCl_2 \cdot 6H_2O$	3.3616	g/l
$MgCl_2 \cdot 6H_2O$	0.9447	g/l
KCl	3.1079	g/l
$SrCl_2 \cdot 6H_2O$	0.1978	g/l
$BaCl_2 \cdot 6H_2O$	1.3969	g/l
$NaCl$	70.3995	g/l
$NaHCO_3$	2.2785	g/l
TRUE Na	28318.366	mg/l
CHLORIDE	46,000	mg/l

TABLE 4

Results from C-Ring SCC Tests, At 80°C and 100% of the 0.2% Proof Stress

ALLOY	H_2S PRESSURE (BAR)		
	0.125	0.25	0.375
UNS S31803	No Crack/ Fine Crack	Crack/Crack	Several Cracks/ Several Cracks
UNS S31200 (High Mo)	No Crack/ No Crack	Pits and Fine Cracks/ Pits and Fine Cracks	Several Cracks/ Several Cracks
UNS S32760 (Cold Worked)	No Crack/ No Crack	No Cracks/ No Cracks	No Cracks/ No Cracks
UNS S32760 (Sol Annealed)	No Crack/ No Crack	No Cracks/ No Cracks	No Cracks/ No Cracks

TABLE 5

Results of Pitting Corrosion Tests At 121°C

ALLOY	H_2S PRESSURE (BAR)		
	0.125	0.25	0.375
UNS S31803	No Pits	No Pits	Deep Pitting (>0.5mm) Both Samples
UNS S31200 (High Mo)	No Pits	No Pits	Deep Pitting (>0.5mm)/ 3 Shallow Pits
UNS S32760 (Cold Worked)	No Pits	No Pits	No Pits/3 Shallow Pits

TABLE 6

Results of Crevice Corrosion Tests With PTFE Multiple Crevice Washer Assembly AT 121°C

ALLOY	H_2S PRESSURE (BAR)		
	0.125	0.25	0.375
UNS S31803	No Attack	No Attack	6 Segments Attacked
UNS S31200 (High Mo)	No Attack	No Attack	4 Segments Attacked
UNS S32760 (Cold Worked)	No Attack	No Attack	2 Segments Attacked
UNS S32760 (Sol Annealed)	No Attack	No Attack	No Attack

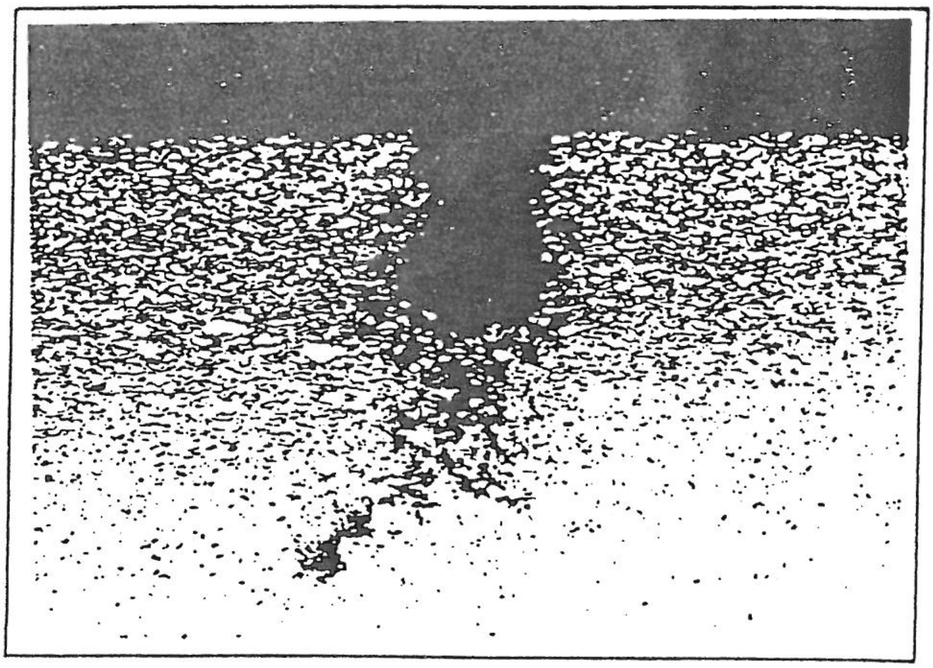

FIGURE 1 - CRACK IN 22Cr C-RING TESTED WITH 0.25 BAR H_2S (X200)

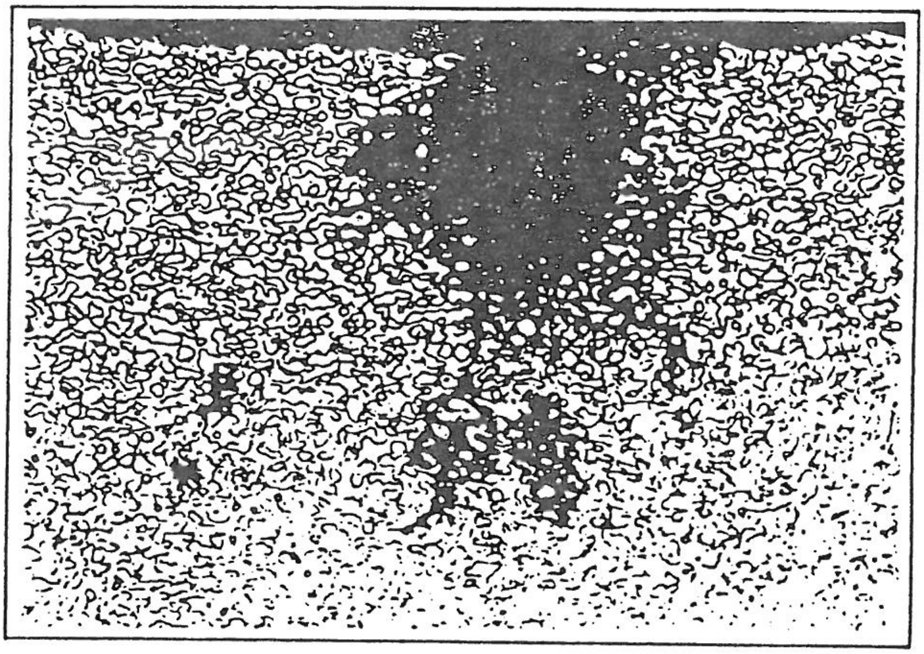

FIGURE 2 - CRACK IN 25Cr C-RING TESTED WITH 0.25 BAR H_2S (X200)

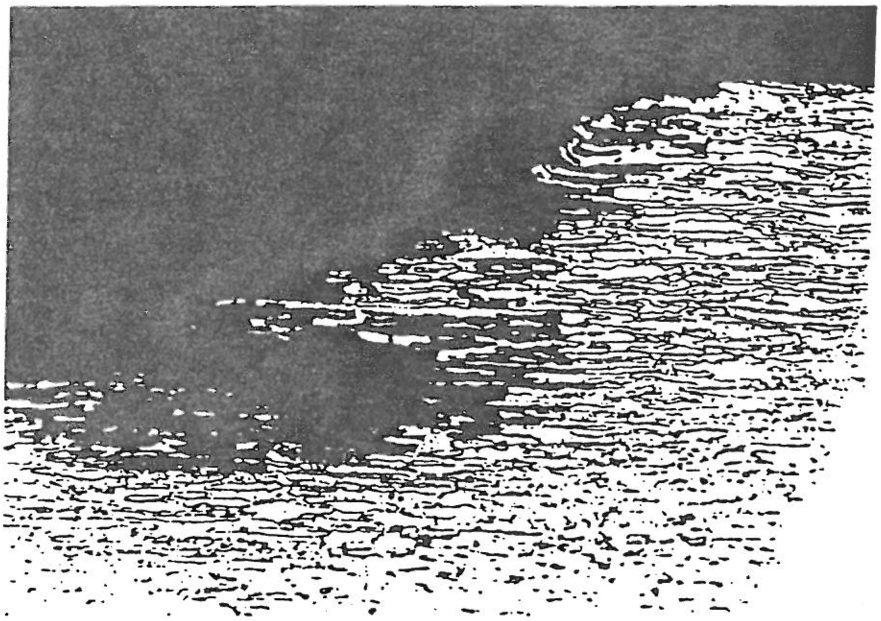

FIGURE 3 - PITTING CORROSION ON 22Cr BENT BEAM SPECIMEN TESTED AT 121°C, 93 BAR CO_2, 0.375 BAR H_2S (X200)

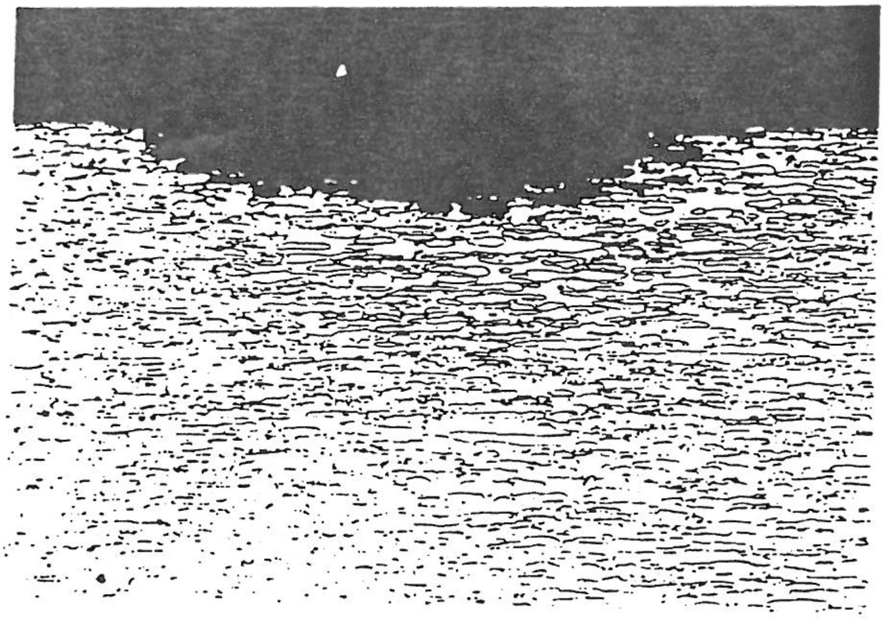

FIGURE 4 - PITTING ON 25Cr BENT BEAM SPECIMEN, TESTED AT 121°C, 93 BAR CO_2, 0.375 BAR H_2S (X 100)

Suggested limits for Duplex stainless steels (pH>4)