Hydrogen embrittlement in cathodically protected super duplex stainless steel

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This paper describes a programme of work set up to investigate the susceptibility of super duplex stainless steels to hydrogen embrittlement under cathodically polarised conditions. Constant load tensile tests have shown that although the material is susceptible to embrittlement, failure only occurs at high stress levels. This behaviour can be attributed to the presence of the austenitic phase which restricts the growth of hydrogen induced cleavage cracks through the ferrite. However under cyclic loading the austenite ligaments fail and hydrogen enhanced crack growth can then progress. As a result fatigue crack propagation rates are markedly higher under cathodic polarisation. This highlights the importance of using suitable test techniques when making an assessment of this phenomenon.

INTRODUCTION

Duplex and super duplex stainless steels are materials that offer an attractive combination of high strength, toughness and corrosion resistance. As a result they have found widespread use in the offshore oil and gas industry. However, as these alloys contain nominally 50% ferrite there is potentially a risk of hydrogen embrittlement if critical combinations of hydrogen content and mechanical stresses and strains are exceeded. The problem lies in identifying the detailed nature of these critical criteria for embrittlement.

In many cases duplex stainless steels are cathodically protected, but until recently service experience had suggested that problems with hydrogen embrittlement were thought to be restricted to cases where either poor welding or processing had resulted in the formation of excessively high ferrite contents. Laboratory tests indicated that cracking only occurred at very low polarisation potentials and very high applied stresses, well above the proof stress and typical design stresses. However as experience in this area has grown and the materials have found increased use in offshore deep-water applications, there has been renewed interest in identifying the factors controlling hydrogen embrittlement in these materials. In deep-water environments protection currents are higher and anode lives shorter due to the absence of calcareous deposit formation. The potential for hydrogen embrittlement is therefore increased and so there is a desire to more precisely define the environmental and mechanical conditions under which this form of embrittlement may be a problem.

Constant stress tensile testing provides a relatively quick and inexpensive method for investigating this phenomenon. However the simplicity of this technique belies the true complexity of the effect being examined. Hydrogen embrittlement in these materials is associated with the development of a cleavage fracture mode through the ferrite phase of the duplex microstructure. It is unlikely that this change in fracture mode can be described solely in terms of a critical macroscopic stress. Stress concentrators may have a significant effect on the resistance of these materials to hydrogen embrittlement as too could the application of a fatigue loading. This paper describes a programme of work dedicated to exploring these issues.

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EXPERIMENTAL

The material used in this investigation was the super duplex grade UNS S32760 in the form of 30 mm thick plate. The microstructure consists of approximately equal volume fractions of ferrite and austenite as shown in Figure 1. A chemical analysis is given in Table 1, along with measurements of basic mechanical properties.

Cylindrical tensile specimens were prepared parallel to the rolling direction with the central gauge length being 4 mm in diameter. Some specimens had an additional 0.1 mm radius V notch applied around the circumference to give a reduced diameter of about 3 mm. Tests were conducted at various applied loads and electrochemical potentials in 3.5 wt% NaCl solutions at ambient temperature.

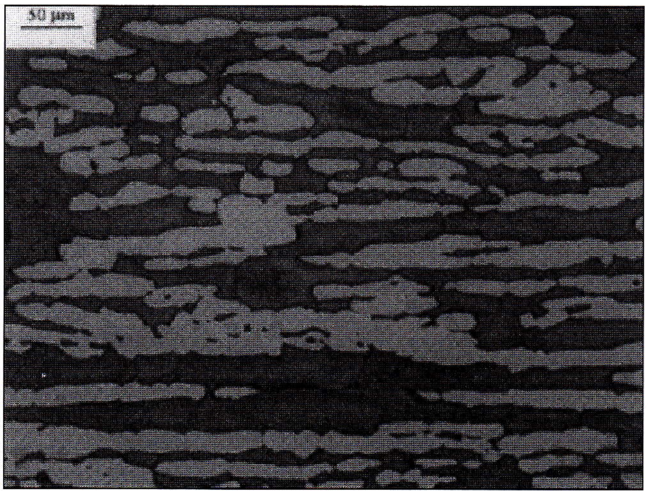

Fig. 1 - Microstructure of UNS S32760 Plate.

Low frequency fatigue crack growth tests have been carried out using a flotation fatigue rig running at a frequency of 0.0083 Hz (2 minutes per cycle). The set-up applies a trapezoidal waveform to a single edge notched bend specimen and crack lengths are monitored using a DCPD technique. The environment used was again 3.5 wt% NaCl solution and tests have been carried out under free corrosion or at –1100 mV(SCE). Stress ratios of zero and 0.5 have been used and all specimens were prepared in the microstructural orientation TL. Testing was supplemented by both optical and scanning electron microscopy to examine sectioned crack paths and fracture surface features when appropriate.

		C	Ni	Cr	Mn	Cu	Si	S	P	Mo	W	N
UNS S32760	min		6.0	24.0		0.5				3.0	0.5	0.2
	max	0.03	8.0	26.0	1.0	1.0	1.0	0.01	0.03	4.0	1.0	0.3
	actual	0.01	7.73	25.0	0.84	0.60	0.31	0.0009	0.025	3.66	0.58	0.22

Properties	0.2% Proof Stress (MPa)	Tensile Strength (MPa)	Elongation (%)
Specification	>550	>750	>25
Actual	560	794	40.2

Table 1 - Chemical Composition and Basic Mechanical Properties of UNS S32760 Plate.

RESULTS AND DISCUSSION

The effect of electrochemical potential on the behaviour of material held at constant load is shown in Figure 2. For specimens held at 130% of the proof stress all specimens (which were unnotched) failed at potentials of –900 mV(SCE) or lower. The shorter failure times at more negative potentials can be associated with enhanced rates of hydrogen evolution.

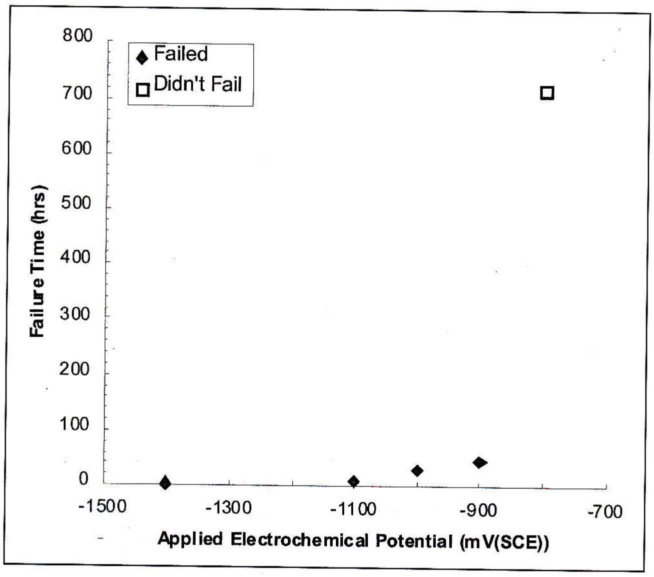

Fig. 2 - Effect of Potential on Failure Time for Specimens Loaded to 130% Proof Stress.

The effect of stress is shown in Figure 3 for both unnotched and notched specimens. In these tests the electrochemical potential was held at –1100 mV(SCE). For the unnotched samples failure occurred when the applied stress was 120% of proof stress or higher. In the notched samples loads were expressed in terms of the fraction of limit load based on the reduced specimen diameter. Failure occurred at loads of 125% limit load or higher. The failure of samples at these stresses is in contrast to the results of similar work [1], although there were differences in the experimental set-ups used.

Examination of specimen fracture surfaces revealed the presence of a transgranular cleavage fracture mode in the region of material around the specimen circumference. On the unnotched specimens numerous cracks were also seen along the parallel length of the specimen, with metallographic sectioning revealing that cracks ran through the ferrite phase and arrested at ferrite-austenite grain boundaries (Figure 4). The results confirm that under these conditions hydrogen cracking can occur, although only at high stress levels. Furthermore the introduction of a circumferential notch did not appear to significantly affect this performance.

However, care should be taken when interpreting this data. Rates of hydrogen diffusion in duplex stainless steels are very low [2,3] and so within the timescale of laboratory testing it is not possible for thermodynamic equilibrium to be reached across the entire specimen diameter. Furthermore the criterion for hydrogen induced cleavage is unlikely to be as simple as merely a critical stress, or even critical local stress. Models for cleavage fracture usually also involve a critical local strain term or a critical local stress triaxiality

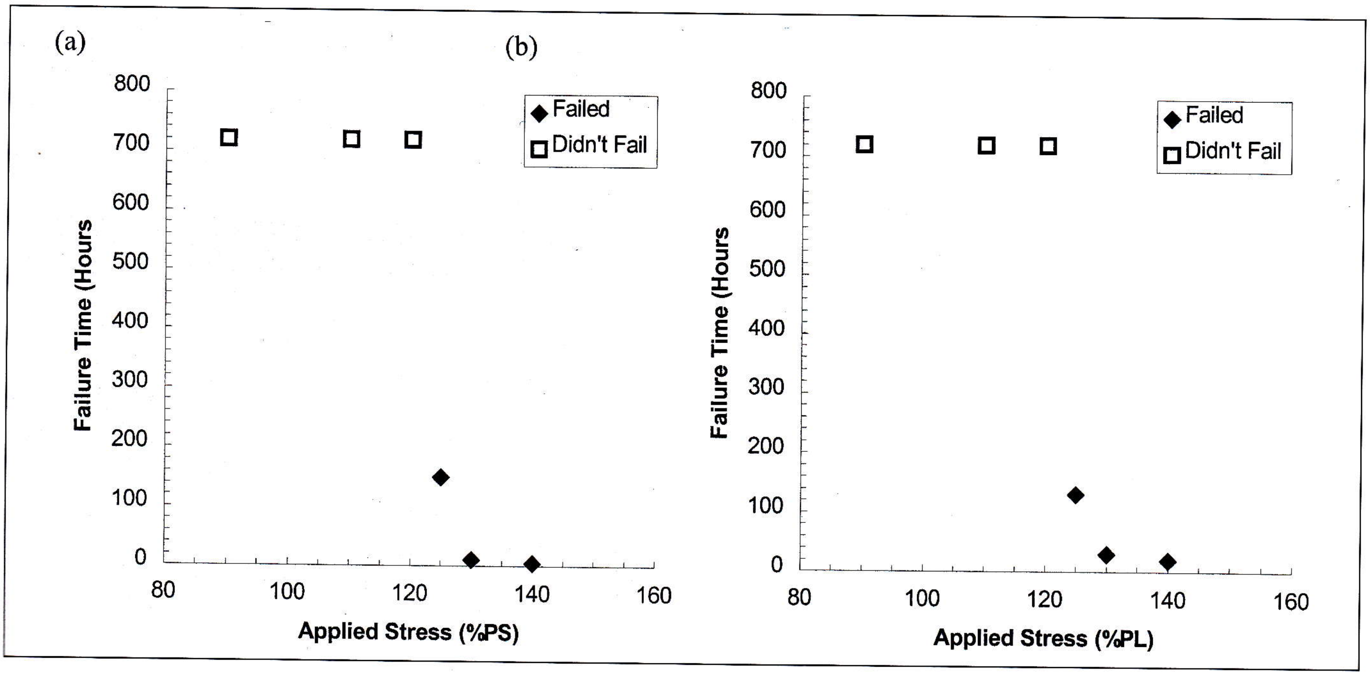

Fig. 3 : Effect of Stress on Failure Time for Specimens Held at –1100 mV(SCE). (a) Unnotched and (b) Notched.

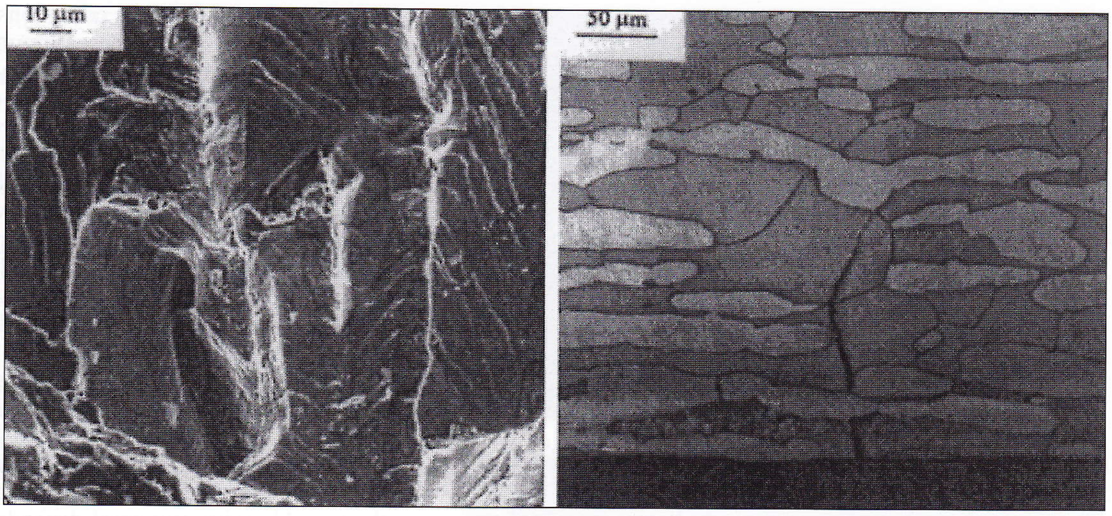

Fig. 4 - Transgranular cleavage through the ferrite phase at the specimen outer surface.

[4,5]. It is likely therefore that a change in specimen geometry may lead to a change in susceptibility. A finite element study may provide a useful way of interpreting results although this process is itself complicated by the fact that these materials are likely to undergo a degree of low temperature creep under these conditions.

The test technique also takes no account of any cyclic loading that may occur in service. This situation is more severe than that used in constant load tensile testing for a number of reasons. From a mechanical standpoint any plasticity ahead of flaws is likely to result in cyclic hardening which will increase the peak stress encountered ahead of the crack. Rates of hydrogen uptake are also likely to be higher as dislocation sweep-in will occur. Ripple load tests have been reported in [6] which showed that a 20 MPa cyclic stress did not effect the performance of tensiles held at 95% UTS. However, this test again used an unnotched specimen. To examine the effect of localised cyclic plasticity on the resistance of these materials to hydrogen embrittlement, low frequency corrosion fatigue tests have been carried out, with the results shown in Figure 5.

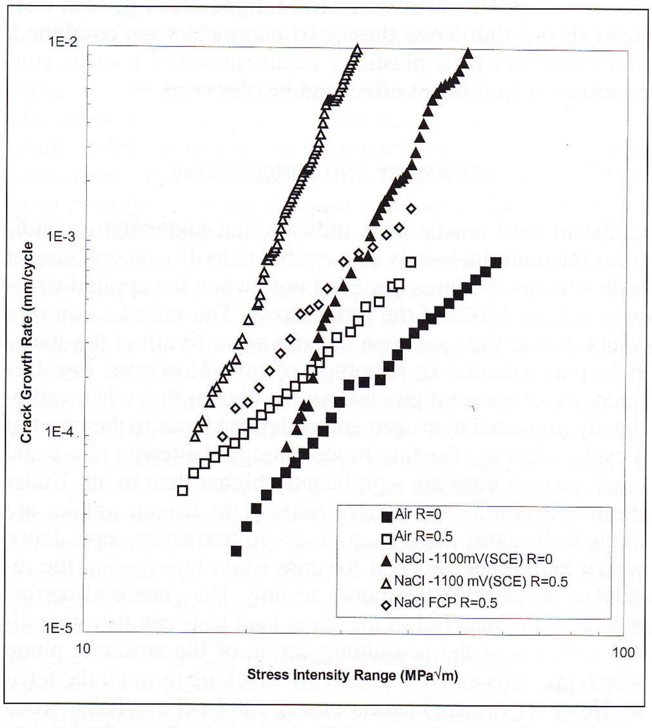

Fig. 5 - Effect of Environment and Stress Ratio on Fatigue Crack Growth Rate.

It can be seen that in air crack growth rates are slightly dependent on stress ratio, as reported in other work [7]. Examination of fracture surfaces revealed that crack growth occurred via a ductile transgranular mechanism, Figure 6. Crack growth rates in sodium chloride solution were higher than in air, even under free corrosion conditions, although the effect was dramatically increased when the specimens were polarised to –1100 mV(SCE). This was accompanied by the appearance of cleavage facets marked by brittle striations, Figure 7. Striation spacings were typically a few microns across and tended to decrease as the crack front approached islands of austenite. The area fraction of cleavage tended to increase with increasing ΔK within each test, and was higher for tests carried out at R=0.5 than those at R=0.

Under free corrosion conditions the effect of testing in sodium chloride solution is only slight. This agrees with other work where the increase in crack growth rate was never more than a factor of two and was only seen over a narrow range of applied ΔK [8]. This was attributed to slow hydrogen entry kinetics under these conditions which prevented an effect being seen at high crack growth rates. In the current work the effect seems to be maintained over a larger range of ΔK and this could be associated with the lower test frequency used in this work (0.008 Hz as opposed to 0.1 Hz).

At an applied electrochemical potential of –1100 mV(SCE) crack growth rates were further enhanced across the entire range of ΔK investigated. This can be attributed to an increased supply of hydrogen under these conditions which allows the region of material ahead of the crack tip to attain equilibrium more readily. Crack growth rates were higher than in similar tests described in other work [6] although this could

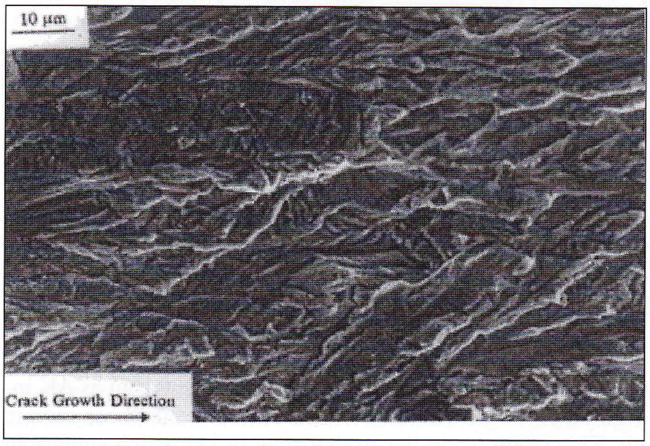

Fig. 6 - Fracture Surface Appearance when Tested in Air.

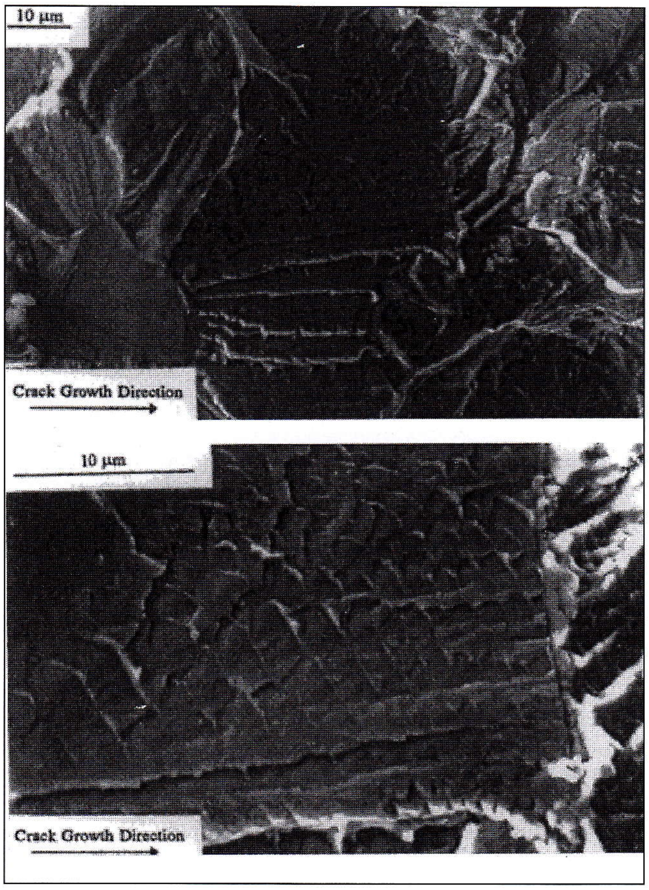

Fig. 7 - Fracture Surface Appearance when Tested in NaCl.

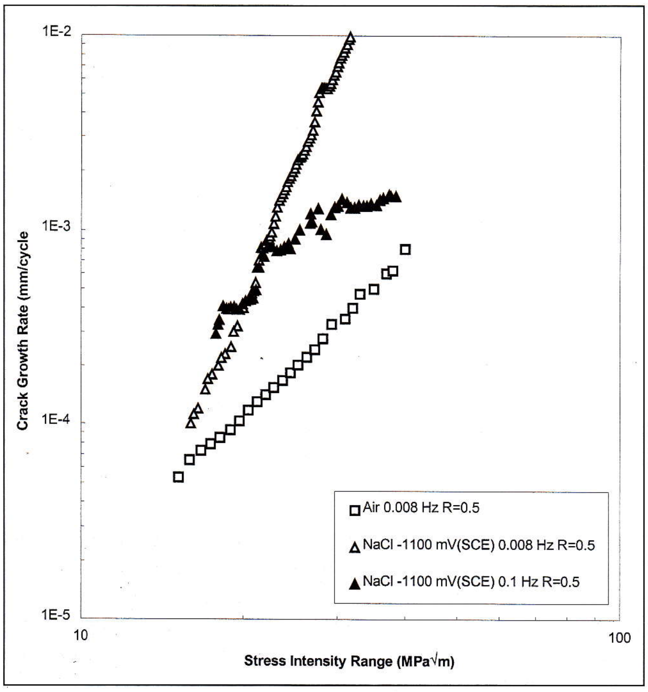

Fig. 8 - Effect of Test Frequency on Fatigue Crack Growth Rate.

again be associated with the much lower test frequency used in this work. To investigate the effect of frequency a test was carried out under similar conditions at 0.1 Hz, with the results shown in Figure 8. Crack growth rates were initially similar to those seen in the lower frequency tests, but as ΔK increased crack growth rates tended back towards those seen in air. This result is similar to that seen in [8] which suggested that under these conditions hydrogen entry kinetics were too slow to allow equilibrium conditions to be maintained at high growth rates. Under these circumstances it is realistic to expect crack growth rates to show a frequency dependence, and the results shown in this work seem to support this view. By contrast, work looking at fatigue behaviour in hydrogen gas has shown that crack growth rates can be insensitive to frequency [8]. Within the range of frequencies investigated (0.1 Hz to 5 Hz) crack growth rates were similar and this was attributed to rapid hydrogen uptake under these conditions with the near crack tip region readily attaining equilibrium. Under such conditions the obtained crack growth rate can be thought of as representing an upper bound. The growth rates obtained at 0.008 Hz in this work are close to the upper bound data generated in hydrogen gas [8]. It may therefore be that by lowering the test frequency we have ensured the attainment of equilibrium conditions within the critical crack tip region. However, only by testing at still lower frequencies could this hypothesis be tested. Perhaps more important is the possible microstructural dependence of the upper bound itself. Variables such as microstructural orientation and ferrite volume fraction (particularly in weld heat affected zones) are likely to have an important effect [9].

Stress ratio is also shown to have a significant effect. Crack growth rates at R=0.5 were significantly higher than those seen at R=0. This was associated with a higher area fraction of cleavage under these conditions. Previous work has suggested that the area fraction of cleavage is controlled by K_{max} [10] and these results seem to exhibit the same dependence. From the results at R=0 it seems that there may be a critical value of K_{max} below which no ferritic cleavage occurs and no increase in crack growth rate is seen, although data in this low ΔK regime could not be collected due to the low crack growth rates involved.

The resistance of this material to hydrogen embrittlement under cathodic polarisation is therefore shown to be critically dependent on the test method chosen for the investigation. When testing under constant load the presence of the austenite phase restricts the extent of hydrogen induced cracking through the ferrite. The introduction of a stress concentrator seems to have no effect on the materials behaviour under these conditions. With unnotched specimens the application of a cyclic load has likewise been shown to have no effect [6]. However corrosion fatigue crack growth tests have shown that when these two parameters are combined, and localised cyclic plasticity occurs ahead of a stress concentrator, a significant effect can be observed.

SUMMARY AND CONCLUSIONS

Constant load tensile tests indicate that under these conditions the material is only susceptible to hydrogen cracking at high stresses. Failures occurred only when the applied stress was at least 120% of the proof stress. The introduction of a V notch into the specimen did not seem to affect the materials performance in this type of test. However, low frequency corrosion fatigue testing has shown that when cathodically protected hydrogen embrittlement leads to the onset of a cyclic cleavage fracture mode through the ferrite phase and crack growth rates are significantly higher than in air. Under these test conditions, where rates of hydrogen uptake are likely to be slow, there is an observed frequency dependence which highlights the need for care when interpreting the results of accelerated laboratory testing. The enhanced performance of the material in the static load tests can be rationalised in terms of the restraining action of the austenite phase which prevents extensive cleavage cracking through the ferrite. However the application of a cyclic load inevitably leads to failure of the austenite itself which then allows further hydrogen enhanced crack growth through the ferrite.

REFERENCES

[1] P Olsson, A Delblanc Bauer and H Eriksson, Hydrogen embrittlement of duplex grades UNS S32750 and UNS S31803 in connection with cathodic protection in chloride solutions, Duplex Stainless Steels '97 [Proc Conf], Maastricht, The Netherlands, 21-23 October 1997, pp. 607-618.

[2] A Turnbull and A J Griffiths, Implications of hydrogen uptake and transport for environment assisted cracking testing and interpretation of results, British Corrosion Journal, Vol. 31 (1996), No. 1, pp. 39-43.

[3] A Turnbull and R B Hutchings, Analysis of hydrogen atom transport in a two-phase alloy, Materials Science and Engineering, A177 (1994), pp. 161-171.

[4] M Wall et al., Fracture criteria for hydrogen and temper embrittlement in 9Cr1Mo steel, Acta Metall. Mater., Vol. 42 (1994), No. 4, pp. 1295-1309.

[5] J H Chen et al., Further study on the mechanism of cleavage fracture at low temperatures, Acta Metall. Mater., Vol. 42 (1994), No. 1, pp. 251-261.

[6] R Francis et al., Effects of cathodic protection on duplex stainless steels in seawater, Corrosion, Vol. 53 (1997), No. 3, pp. 234-240.

[7] T J Marrow and J E King, Fatigue crack propagation mechanisms in a thermally aged duplex stainless steel, Materials Science and Engineering, A183 (1994), pp. 91-101.

[8] T J Marrow and J E King, Microstructural and environmental effects on fatigue crack propagation in duplex stainless steels, Fatigue Fract. Engng Mater. Struct., Vol. 17 (1994), No. 7, pp. 761-771.

[9] W Zheng and D Hardie, Effect of structural orientation on the susceptibility of commercial duplex stainless steels to hydrogen embrittlement, Corrosion, Vol. 47, No. 10, pp. 792-799.

[10] T J Marrow, C A Hippsley and J E King, Effect of Mean Stress on Hydrogen Assisted Fatigue Crack Propagation in Duplex Stainless Steel, Acta Metall. Mater., Vol. 39, No. 6, pp. 1367-1376.

ABSTRACT

INFRAGILIMENTO DA IDROGENO DI ACCIAIO INOSSIDABILE SUPERDUPLEX CATODICAMENTE PROTETTO IN ACQUA MARINA NATURALE

Gli acciai inossidabili duplex e superduplex sono materiali che offrono una favorevole combinazione di caratteristiche quali l'elevata resistenza, la tenacità e la resistenza alla corrosione. Pertanto trovano un largo impiego nell'industria petrolifera, negli impianti offshore e di distribuzione del gas. Tuttavia, poiché queste leghe contengono nominalmente il 50% di ferrite esiste potenzialmente il rischio di un infragilimento da idrogeno se si superano condizioni critiche determinate da combinazioni sfavorevoli del contenuto di idrogeno e delle tensioni o deformazioni. Il problema consiste nell'identificare i termini di questa combinazione di fattori che risultano essere critici per l'infragilimento.

In molti casi l'impiego di leghe duplex è accompagnato dall'utilizzo di un sistema di protezione catodica. La polarizzazione catodica può aver luogo sia per accoppiamento galvanico ad un acciaio al carbonio sia mediante corrente imposta se il materiale è utilizzato in ambienti ostili in cui la corrosione localizzata può rappresentare un problema. Fino a un periodo relativamente recente, l'esperienza in servizio con questi materiali aveva suggerito che il comportamento degli acciai inossidabili duplex sotto polarizzazione catodica non era di particolare interesse, e si pensava che i problemi fossero ristretti a casi in cui una saldatura o una lavorazione non accurata potessero dar luogo alla formazione di contenuti di ferrite molto alti. Esami di laboratorio hanno indicato che le criccature si verificava solo in presenza di potenziali di polarizzazione molto bassi e sollecitazioni molto alte, molto al di sopra delle sollecitazioni di prova e sollecitazioni tipiche previste nel progetto. Tuttavia studi recenti suggeriscono che il materiale microstrutturalmente privo di difetti può essere suscettibile a infragilimento a livelli macroscopici al di sotto delle sollecitazioni ammissibili, se localmente la sollecitazione uguaglia o eccede leggermente tale sollecitazione. Nella presente memoria si vogliono perciò definire in modo più preciso le condizioni ambientali e meccaniche nelle quali questo modello di infragilimento può costituire un problema.

Le tecniche tradizionali utilizzano campioni tensili cilindrici a lati squadrati che vengono sottoposti sia a carichi costanti che a carichi leggermente crescenti. Esse permettono di effettuare prove relativamente veloci ma sono generalmente considerate troppo severe a causa delle eccessive tensioni che si sviluppano.

Le prove con carichi costanti richiedono tempi lunghi, specialmente con questi materiali che presentano una velocità di diffusione dell'idrogeno molto bassa. Pochi lavori di ricerca su questi materiali sono stati mirati all'investigazione degli effetti della concentrazione delle sollecitazioni o del carico ciclico sull'infragilimento.

Il presente lavoro descrive un programma di lavoro dedicato allo studio del problema. Sono stati effettuate prove per esplorare gli effetti della geometria dei campioni e del profilo del carico sulle prestazioni di queste leghe in condizioni di polarizzazione catodica.