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THE ROLE OF ENVIRONMENTAL AND METALLURGICAL VARIABLES ON THE RESISTANCE OF DUPLEX STAINLESS STEELS TO SULPHIDE SCC

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ABSTRACT

Duplex and super duplex stainless steels are widely used by the Oil and Gas industry for handling slightly sour process fluids. These alloys have limits, beyond which sulphide stress corrosion cracking (SSCC) is likely. In NACE MR0175 the operating limits of alloys are usually defined by a maximum hardness and an H_2S limit. For one or two alloys another parameter may also be specified. The present paper has collected together a body of evidence, some of it previously unpublished, to show that the susceptibility to SSCC depends on a number of environmental variables, ie. temperature, chloride, pH and H_2S, as well as several metallurgical variables eg. microstructure and degree of cold work. The data for one alloy, a proprietary super duplex stainless steel, is used to show how these variables inter-relate, and where the alloy may be safely used. The results clearly show that NACE MR0175 is inadequate for specifying the limits of use of a duplex or super duplex stainless steel. The authors suggest that where an alloy is thought likely to be useful and the conditions are outside the scope of MR0175, testing as specified in the European Federation of Corrosion document on CRA's (Publication No. 17), should be carried out.

INTRODUCTION

As process streams in Oil and Gas recovery become ever more corrosive, there is an increasing use of corrosion resistant alloys (CRA). These include martensitic, ferritic, austenitic and duplex stainless steels as well as nickel and titanium alloys. One of the most popular alloy types for post wellhead applications is duplex stainless steel, and thousands of tonnes have been used to date. The concern with all CRA's in sour conditions is the possibility of sulphide stress corrosion cracking (SSCC).

The selection of materials resistant to SSCC is covered by NACE MR0175. This document was originally developed for carbon and low alloy steels and with the introduction of CRA's these have had to be incorporated into the document. Originally these were admitted with the same kind of testing as for carbon steels. With time it became apparent that CRA's are affected by environmental and metallurgical variables in a different way to carbon steel. This is reflected in the wording for later additions of CRA's to MR0175, where in addition to an H_2S and hardness limit there may be a chloride and/or a temperature limit. However, these entries still do not reflect the full effect of environmental and metallurgical variables on the resistance of CRA's to SSCC. The aim of the present paper is to show the effect of a number of important variables in the light of the latest data, and to show how the limits of use can be greatly extended.

ALLOYS

The present paper concerns itself with just one group of CRA's; the duplex stainless steels. Many of the variables discussed below also affect the performance of other CRA's, however, in most cases these alloy types are not so well researched as the duplex alloys, and the data is more sketchy.

Table 1 shows the composition of the most common duplex stainless steels. The 22Cr duplex, UNS S31803, has been in service for over 15 years. Ferralium* UNS S32550 was one of the early 25Cr duplex alloys, but these have largely been superseded by the more highly alloyed super duplex stainless steels. Of these S32760 is the only alloy to guarantee a minimum PREN (pitting resistance equivalent number) in excess of 40. The PREN is an empirical relationship which gives a guide to the resistance of stainless steels to localised attack in the presence of chlorides. The PREN is usually derived from the chromium, molybdenum and nitrogen content of the alloy but other versions also include tungsten.

The UNS numbers in Table 1 cover quite a wide range of composition for each alloy. However, proprietary alloys are most usually made to a tighter melting specification and a controlled metallurgy. This can have a significant effect on the corrosion resistance, as described below.

The data presented below is largely concerned with the alloy Zeron 100** (UNS S32760) developed and marketed by the authors' company, and it should be recognised that this is a proprietary alloy with tight control of specifications and that similar properties may not be achieved by uncontrolled S32760 alloys.

ENVIRONMENTAL VARIABLES

NACE MR 0175 is concerned mostly with the H_2S concentration which causes SSCC. However, there are other environmental variables which also affect the susceptibility to cracking. The three most important are discussed below.

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Temperature

It has been recognised for some time that the temperature for least resistance to cracking varies from alloy group to alloy group. For duplex stainless steels the critical temperature is generally found to lie in the range 70^0 to 110^{0}C. Barteri (1) reviewed data from a number of sources for solution annealed and cold worked duplex alloys. Figure 1 shows data for both 22Cr and 25Cr alloys in the solution annealed or lightly cold worked condition (~ 825 MPa [125ksi] 0.2% proof stress). The curves show either a minimum in the range 70^0 to 100^{0}C or they are approximately flat. Cottis & Newman (2) have suggested that this variability is caused by differences in the test methods and environmental conditions used by the different laboratories.

The results (Figure 2) for heavily cold worked material (≥ 960 MPa [140ksi] 0.2% proof stress) show that the resistance to SSCC decreases slightly as the temperature increases, with no minimum at intermediate temperatures. The results also show that for 25Cr duplex alloys the heavily cold worked material is considerably more susceptible to SSCC than the solution annealed alloy.

Thus it is clear that the environmental variable of temperature is closely linked to a metallurgical variable ie. cold work.

Chloride

The effect of chlorides on SSCC resistance is not so well known as that of, say, temperature. However, there is an increasing body of data to show that the performance of many classes of CRA is affected by the chloride concentration in the process fluids. Gooch et al (3) surveyed a large number of references concerning SSCC tests of 22Cr duplex stainless steel. Although these used a wide range of test methods and environmental conditions there was a clear trend of increasing H_2S limit for cracking as the chloride concentration decreased. However, the large spread of data makes the setting of absolute limits difficult. Some of the spread is probably due to variations in composition possible with this alloy, as described below.

Figure 3 shows some results for the authors' company's proprietary super duplex in the lightly cold worked condition (hardness 34 to 35 HRC). All tests were in unbuffered brines containing 18 to 25 bar of CO_2, and in the temperature range 80^0 to 100^{0}C. The partial pressures of CO_2 and H_2S gave pH's in the range 3.3 to 3.6, at temperature and pressure, calculated using the nomogram of Bonis & Crolet (4). All the tests were on C-rings stressed to 100% of the actual 0.2% proof stress using the methods described in EFC publication no. 17 (5), ie using strain gauges on the C-rings and deriving the required strain from a tensile stress-strain curve for the material. The data show that a decrease of the chloride content by a factor of ten increases the H_2S limit also by about a factor of 10. This offers substantial extension of the use of super duplex for sour brines with lower chloride contents.

In areas such as gas condensate lines the chloride concentration will not exceed about 1000 mg/l (5) and hence this alloy may be capable of resisting SSCC at even greater H_2S concentrations under these conditions.

Figure 4 shows the MR0175 limit for S32760 compared with the data from Figure 3. This clearly demonstrates the over conservatism of MR0175.

pH

The pH of oil field brines has been discussed in detail by Bonis & Crolet (4). It is controlled principally by the acid gases H_2S and CO_2, and the temperature. In real brines this typically gives pH's of 3 to 4. The pH can be modified by the presence of buffers, the most common of which are bicarbonate and acetate. Bicarbonate in a formation water typically gives pH values in the range 4 to 5.5.

There is little data on the effect of pH on SSCC under typical service conditions. Spähn (6) presented data on the time to failure of 22Cr duplex from pH 3 to pH 8. The time to failure increased with pH, but the test environment was very severe ie. 4.3M NaCl with 1 bar H_2S.

Oredsson et al (7) tested heavily cold worked 22Cr duplex in 5% NaCl with 1 bar H_2S. Samples were stressed to the 0.2% proof stress and the pH was controlled by acetate additions. At 90°C the H_2S limit was ~ 0.03 bar at pH 2.5 and 0.6 bar at pH 3.9. This data suggests that an increase of pH of 1 unit increases the H_2S limit by at least one order of magnitude. However, further data is required to confirm this effect of pH over a wider range. The effect of pH is clearly important in SSCC limits for CRA's and yet it is mentioned for only one alloy in MR0175 - 96.

METALLURGICAL VARIABLES

There are many metallurgical variables which could be examined. However, the four discussed below are the most relevant for duplex stainless steels.

Composition

It seems obvious that the more highly alloyed a CRA is the more resistant it should be to SSCC. SSCC of duplex stainless steels requires the initiation of localised corrosion for a crack to develop (2). Hence the more resistant an alloy is to pitting in sour brines, the more resistant it will be to SSCC. Francis and Byrne (8) showed that in a range of sour brines, the more highly alloyed a duplex stainless steel was, the more resistant to SSCC and pitting it was. The super duplex alloy S32760 did not crack in any of the test environments while 22Cr duplex and a lower alloy 25Cr duplex material did.

Another aspect of this is the fact that the UNS composition limits for many alloys are quite wide. For instance, a 22Cr duplex which is lean in chromium, molybdenum and nitrogen could have a PREN as low as 28, while an alloy at the upper limit would have a PREN of 37. This range of composition clearly would be expected to have an effect on the resistance to SSCC. It is for this reason that manufacturers of proprietary alloys use a much tighter melting specification than that in the UNS standard.

Further testing to show the effects of composition variations has commenced, but data is not yet available.

Phase Balance

Modern duplex stainless steels are made to a nominal phase balance of 50/50, and the majority of alloys fall within the range 40% to 60% ferrite. Excursions outside these limits, say to 30% or 70% ferrite will have an impact on SSCC resistance. The mechanism by which the two phases in duplex stainless steels interact to prevent the propagation of cracks is discussed by Cottis & Newman (2).

Alloys with low ferrite contents will not only have an austenite phase removed from its optimum composition, but they will also become more susceptible to cracking in high chloride brines. Similarly alloys with high ferrite contents will also have non-optimum element partition between the phases and such an alloy will be more susceptible to cracking where hydrogen embrittlement is the primary crack propagation mechanism (2).

The biggest variation in phase balance is seen with welds. Using best current practice the ferrite content of as-welded deposits is usually 40% - 60% ferrite. Occasionally a weld with 65% ferrite is seen. Welds with 70% or more ferrite are much more susceptible to environmental cracking. Tests on such welds in sour brines have not been reported, but welds in 22Cr duplex with 70% or more ferrite have proved susceptible to chloride SCC at temperatures around 100^0C (9).

Table 2 summarises a large range of SSCC tests on as-welded test pieces in the authors' company's proprietary super duplex. All of these had ferrite contents in the normal range and proved resistant to cracking.

Cold Work

The effect of cold work was touched on above when discussing the effect of temperature. A number of authors have pointed out that solution annealed material is more resistant to SSCC than cold worked (eg 1,7).

Oredsson et al tested 22Cr duplex with different levels of cold work in 5% NaCl +0.5% acetic acid at 90^0C, with different levels of H_2S. The results in Figure 5, clearly show the effect of increasing levels of cold work on the H_2S level at which SSCC occurs.

The authors' have carried out autoclave tests on C-rings of their company's proprietary super duplex. The samples were in three different conditions; solution annealed, cold worked to a proof stress of >750 MPa, and girth welds in solution annealed material, all tested in duplicate. The results, summarised in Table 3, show that, under the test conditions, an increase from 1.3 to 1.8 bar H_2S caused cracking of the cold worked material, while solution annealed and welded material were satisfactory. It should be noted that the cold worked material which was tested had a 0.2% proof stress of 945MPa (137ksi), which is well in excess of that normally occuring with cold worked bar. Cold worked bar has a 0.2% proof stress which is more commonly around 800 MPa (116ksi). Such material may well have resisted SSCC under both the conditions described in Table 3.

Some people have tried to use proof stress as an indicator of cold work. This is unreliable and hardness gives a better correlation. The results of a survey of cold worked bar (1/2" to 2 1/2") in the authors' company's warehouse showed that while hardness generally increases as the proof stress increases, there is a great deal of scatter, making a reliable correlation impossible (Figure 6).

The reason for this is that when bar is cold worked the cold working is not uniform, but tends to be greater in the outer region. A tensile sample is generally substantial in size and hence tends to give an average figure for the increase in strength. However, a hardness measurement is local and is usually made on the outer surface, where the cold work is greatest. As it is the outer surface which is most often exposed to sour environments, eg fasteners, the hardness is a better guide to susceptibility to SSCC than the proof stress.

Third Phases

If duplex alloys are cooled sufficiently slowly between 1000^0 and 800^0C, third phases such as chi and sigma are precipitated. These phases are rich in chromium and molybdenum and leave a denuded zone around themselves. If sufficient third phase is precipitated a network of denuded zones can result, which can lead to reduced corrosion resistance.

Sigma phase is most commonly found in the HAZ of welds in thin wall, small diameter pipe. Generally the concentration, as determined by point counting, is in the range 0.5 to 2 or 2.5%.

The authors carried out autoclave tests on girth welded C-rings in NPS 2 schedule 10S pipe of their company's proprietary super duplex. Welding heat inputs had been increased above normal to produce sigma in the HAZ. All the welds were stressed to 100% of the 0.2% proof stress of the parent pipe adjacent to the weld beads using strain gauges and a strain value derived from the stress-strain curve for the parent pipe, as recommended in EFC publication no. 17 (5). The test conditions are summarised in Table 4. All of the welds showed no signs of cracking or corrosion. After testing the welds were sectioned and the sigma content in the most highly stressed part of the HAZ was determined. The sigma contents ranged from 0 to 2.5%.

This is in agreement with Bowden (10) who also found sigma had no effect on corrosion resistance at levels of 2.5%, but found that the effect of sigma on impact toughness was more important. Even at levels of 2.5%, Bowden achieved adequate impact toughness.

DISCUSSION

It is clear from the data presented above that the SSCC behaviour of duplex stainless steels is controlled by a range of environmental and metallurgical variables. In addition some of these are closely linked, such that a change in one can produce a change in the effect of another variable eg cold work and temperature. Thus when selecting materials it is important to consider all the variables together, rather than picking one or two in isolation.

Many CRA's were admitted into MR0175 as a result of tests on a proprietary alloy with a tightly controlled metallurgy and composition. However, these materials are listed in MR0175 as their UNS numbers which often permit much wider scope for material variation. Hence care is needed in material selection to ensure that all the metallurgical requirements are satisfied.

Testing for entry of CRA's into MR0175 typically involves tests in a high chloride unbuffered brine with CO_2 and H_2S. However, this is a worst cast, ie low pH, high chloride, which is rarely found in practice. The majority of oil field brines fall into one of two categories. One is sour gas where chloride levels are low (<1000 mg/l) and pH's are also low (3 to 3.5). The alternative is a sour formation water with high chlorides, but also containing bicarbonate. This generally has a pH > 4. The data presented above shows that under both of the commonly occurring conditions duplex stainless steels have a much wider range of application than is permitted by MR0175.

The oil and gas industry, like many others, is constantly looking at ways to keep costs down. The selection of duplex or super duplex stainless steels rather than high alloy austenitics or nickel base alloys is one way to achieve this. This has been recognised by the European Federation of Corrosion Working Group on Oil and Gas. Its document on CRA's (5) suggests a review of manufacturers data and advises on methods of testing, both to identify appropriate materials and to ensure uniformity of test methods from laboratory to laboratory. This ensures that reliable, but not overly conservative data is available for materials selection.

All of the data generated by the authors and reported above has been carried out according to the principles of EFC publication no. 17.

CONCLUSIONS

1. There are a number of factors which affect the resistance of duplex and super duplex stainless steels to SSCC.

2. Some of these variables are closely related and a change in one can affect the critical value of another.

3. These variables are not generally addressed by MR0175 which makes CRA selection overly conservative.

4. The effect of environmental and metallurgical variables is recognised by EFC publication no. 17, and this provides a way of evaluating materials to make the most cost effective selection.

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Table 1 Nominal composition of the common duplex stainless steels

UNS No.	Nominal Composition (Wt%)							PREN*	PRENW**
	Fe	Cr	Ni	Mo	N	Cu	W		
S31803	bal	22	5	3	0.2	-	-	34	34
S32550	bal	25	6	3	0.2	2	-	38	38
S32750	bal	25	7	3.6	0.3	-	-	41	41
S39274	bal	25	7	3	0.3	-	2	39	42
S32760	bal	25	7	3.5	0.3	0.7	0.7	>40	42

NOTES: bal = balance

* PREN = %Cr + 3.3 x %Mo + 16 x %N

** PRENW = %Cr + 3.3 x %Mo + 1.65 x %W + 16 x %N

Table 2 Summary of SSCC data on proprietary super duplex stainless steel welds

Chloride (mg/l)	CO2 (bar)	H2S (bar)	Temp. (°C)	Method	Result
0	5.8	0.05	103	U-Bend	No SSCC
46,000	10.5	0.05	103	U-Bend	No SSCC
46,000	52	0.25	103	U-Bend	No SSCC
30,000	0	16	90	Tensile	No SSCC
30,000	20	5	90	Tensile	No SSCC
30,000	20	5	120	Tensile	No SSCC
30,000	25	0.2	102	Ripple	No SSCC
20,000	18	1.8	90	C-Ring	No SSCC
175,000	40	0.1	190	C-Ring	No SSCC

NOTES:

(1) U-Bend stressed to 100% of yield strength(0.2% offset) per ASTM G30.

(2) Tensile test at 450 MPa applied stress for 30 days.

(3) Ripple test cycled from 100% to 50% of yield strength(0.2% offset) at a strain rate of 3x10-6/sec for 30 days.

(4) C-rings per ASTM G38 but stressed to 100% of yield strength(0.2% offset) using strain gauges & strain from stress-strain curve.

Table 3 Results of SSCC tests on proprietary super duplex stainless steel samples at 100% of 0.2% Proof Stress (C-Ring)

Chloride (mg/l)	CO_2 (bar)	H_2S (bar)	Temp. (°C)	Material	Result (duplicates)
20,000	17.2	1.38	90	sol. ann.	No SSCC
				welded	No SSCC
				cold worked	No SSCC
20,000	18.2	1.79	90	sol. ann.	No SSCC
				welded	No SSCC
				cold worked	Cracks

Table 4 Results of SSCC tests at 90°C on proprietary super duplex (welded with high heat input to generate sigma phase)

Chloride (mg/l)	CO2 (bar)	H2S (bar)	Sigma (%)	Method	Result
30,000	25	0.2	0	C-Ring	No SSCC
30,000	25	0.2	0.4	C-Ring	No SSCC
30,000	25	0.2	1.2	C-Ring	No SSCC
30,000	25	0.2	1.2	C-Ring	No SSCC
30,000	25	0.2	2.5	C-Ring	No SSCC

FIGURE 1 Effect of temperature on the H2S limit for SSCC for duplex (Ref 1)

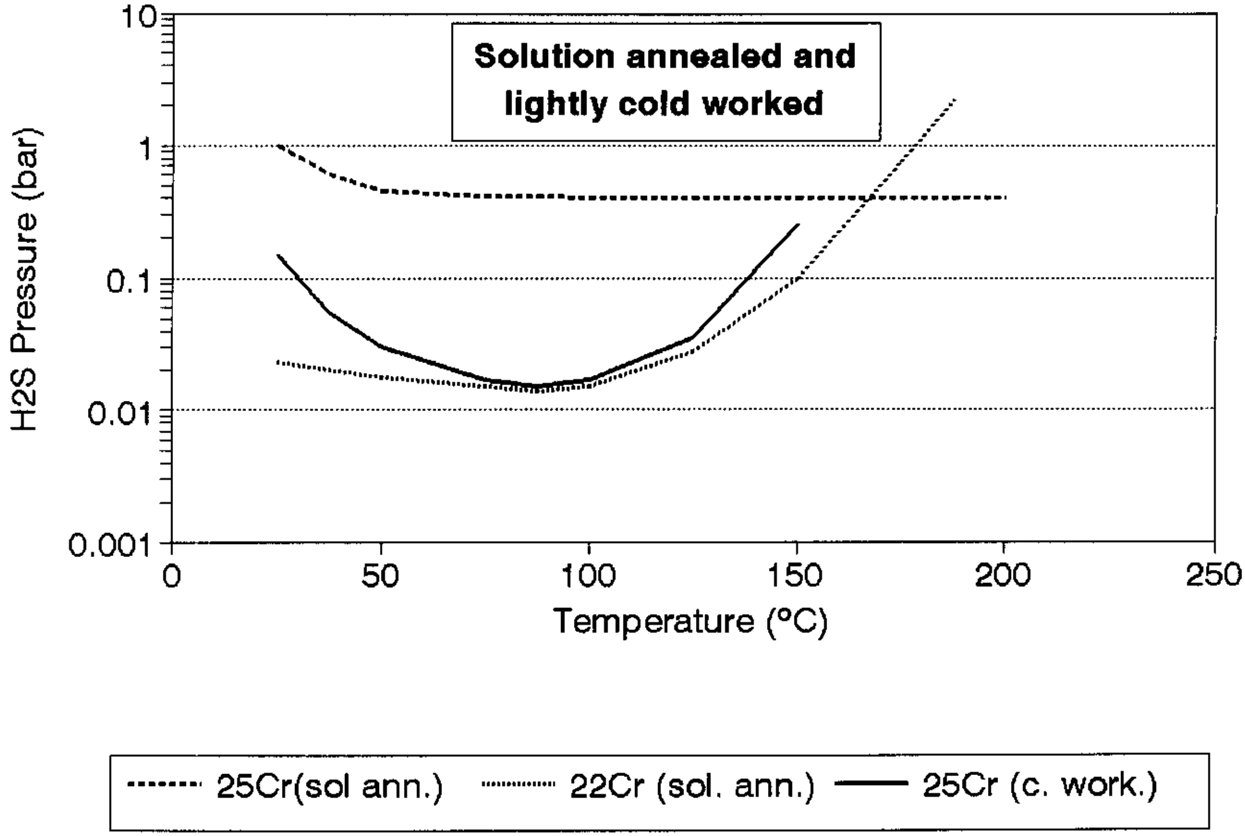

FIGURE 2 Effect of temperature on the H2S limit for SSCC for duplex (Ref 1)

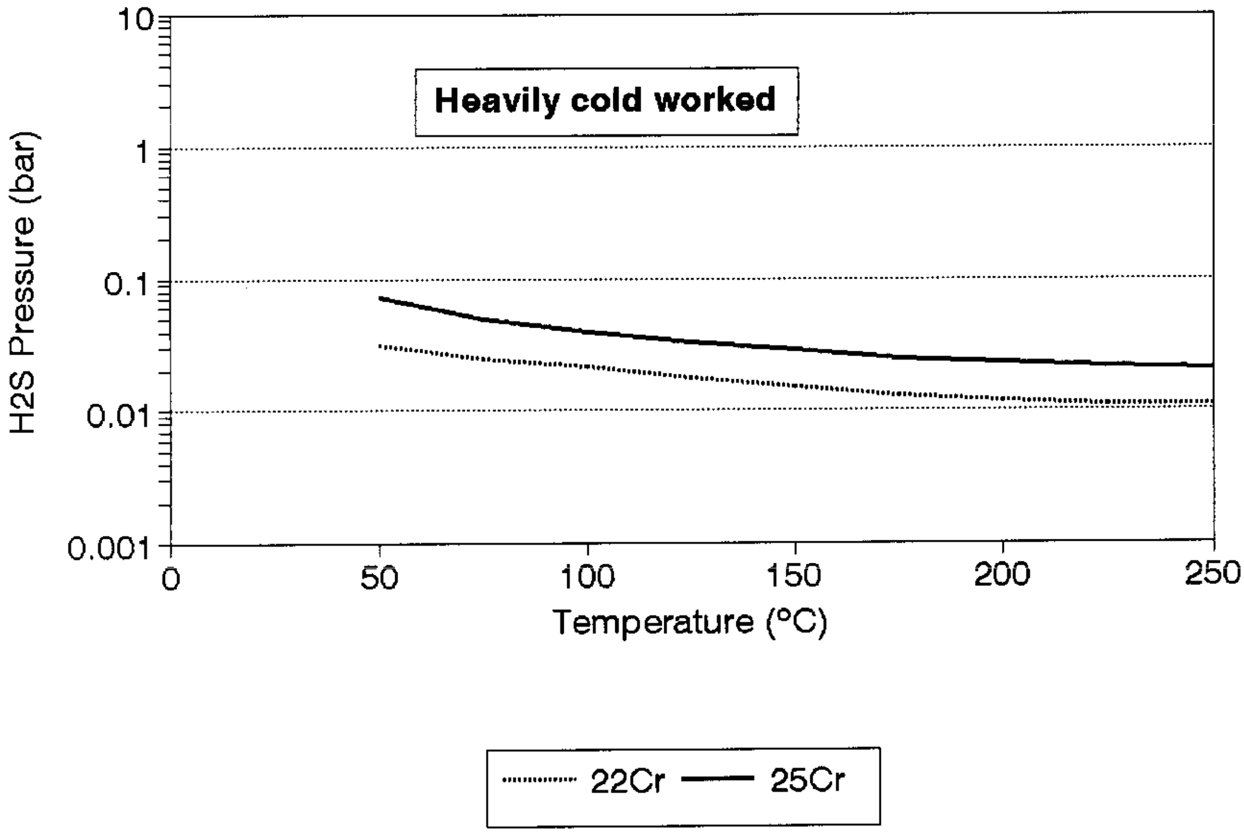

FIGURE 3 SSCC tests on cold-worked proprietary super duplex at pH3 to 4

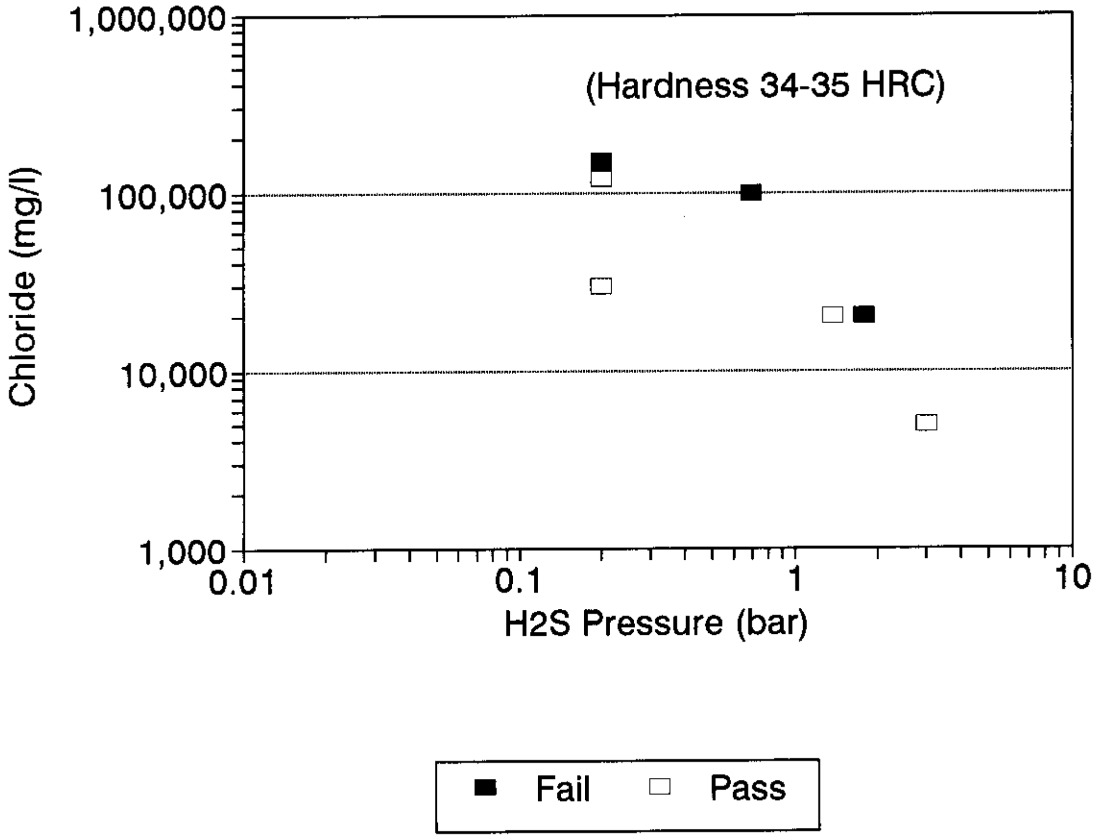

FIGURE 4 Comparison of proprietary SSCC data with NACE MR0175 for UNS S32760

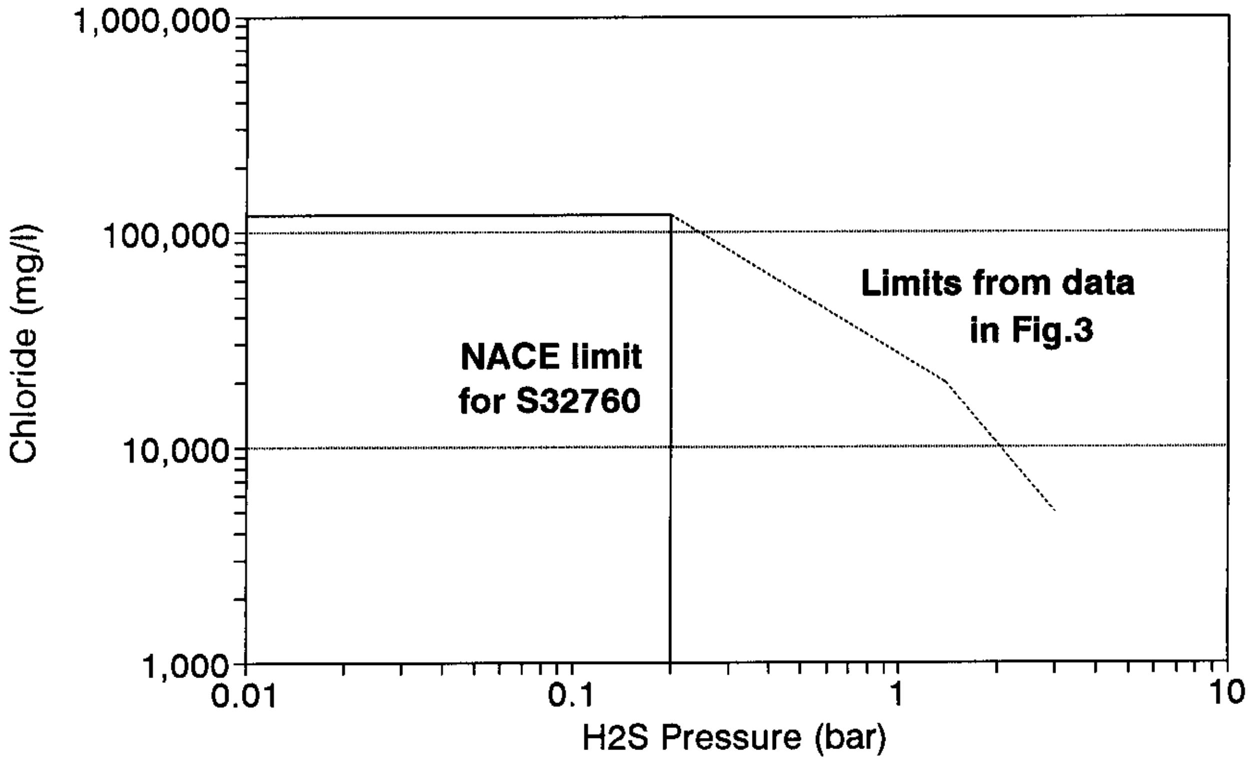

FIGURE 5 Effect of cold work on the H2S limit for 22Cr duplex at 90°C (Ref 7)

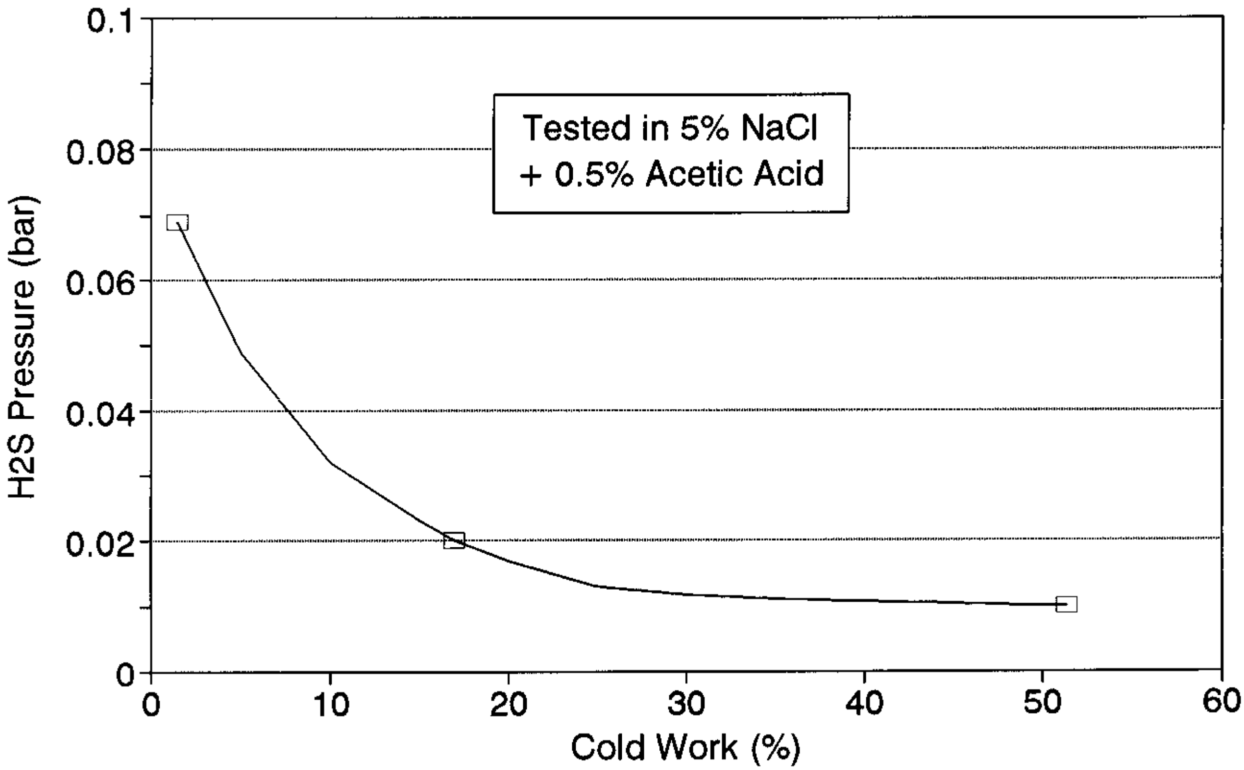

FIGURE 6 Hardness vs 0.2% Proof Stress: cold worked proprietary super duplex