



## REPORT

### THE EFFECT OF TUNGSTEN ON THE PROPERTIES OF SUPER DUPLEX STAINLESS STEELS

**Prepared by:** Roger Francis  
Corrosion Services Manager

**Approved by:** Geoff Warburton  
Technical Director

#### CIRCULATION

<b>Division</b>	Engineering
<b>Job No.</b>	
<b>Reference No.</b>	
<b>Report No:</b>	TN1120R2
<b>Iss No.</b>	2
<b>Date:</b>	Dec 2008

Confidential		Copyright © Rolled Alloys 2008	Rolled Alloys Company Ltd co. registered in USA (Delaware)-#37-1540008, PO Box 1287, Northbrook, Illinois 60065. UK Company Number FC027795 VAT Reg No. GB 803 8704 36
General Release	Y	Rolled Alloys is the owner of the Copyright in this document. The document and its text, images, diagrams, data and information it contains must not be copied or reproduced in whole or in part, in any form or by any means, without the prior written consent of Rolled Alloys	



## THE EFFECT OF TUNGSTEN ON THE PROPERTIES OF SUPER DUPLEX STAINLESS STEELS

### TABLE OF CONTENTS

<u>SECTION</u>	<u>DESCRIPTION</u>
	SUMMARY
1.0	INTRODUCTION
2.0	ALLOYS
3.0	METALLURGY
3.1	Alloy Composition
3.2	Precipitation of Sigma
3.3	Fabrication Experience
4.0	CORROSION
4.1	Seawater
4.2	Oil and Gas Process Fluids
4.3	Chemical Environments
5.0	CONCLUSIONS
	REFERENCES
Table 1	Nominal composition of some commonly used superduplex stainless steels.
Table 2	Some projects which have utilised Zeron 100 superduplex stainless steels.
Figure 1	Typical TTT curve for a superduplex stainless steel (Ref 2)
Figure 2	Charpy impact energy after ageing at 950°C for three superduplex stainless steel welds (Ref 4)
Figure 3	CCT diagram for three superduplex stainless steels for 1% sigma (Ref 5)



- Figure 4 Sulphide SCC limits by SSRT for 25Cr duplex stainless steels (Ref 16)
- Figure 5 ISO corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid
- Figure 6 ISO corrosion curves (0.1mm/y) for some stainless steels in hydrochloric acid



## SUMMARY

The effect of tungsten on the metallurgical structure and the corrosion properties of superduplex stainless steels is discussed. It is concluded that Zeron 100 with 0.5 to 1.0 wt % tungsten gives the optimum microstructure and corrosion resistance.



## 1.0 INTRODUCTION

The 25%Cr duplex stainless steels have been around for over 30 years. In the mid 1980's RA Materials (formerly Weir Materials) introduced Zeron 100, the first of the superduplex stainless steels. These are characterised by higher alloying additions and improved corrosion resistance. The main elements conferring these properties on Zeron 100 are chromium, molybdenum and nitrogen, but the alloy also contains small additions of copper and tungsten as well. Since the successful introduction of Zeron 100, a number of other proprietary superduplex stainless steels have emerged. Some of these contain tungsten, some copper and some neither. The role of copper in duplex stainless steels is fairly well understood (eg. ref 1), however, the role of tungsten is less well understood. Current knowledge shows that tungsten contributes to a number of properties of super duplex stainless steel. The following report summarises the current data on the role of tungsten as it affects the metallurgical structure and corrosion resistance of superduplex stainless steels.

## 2.0 ALLOYS

There are a number of commercial superduplex stainless steels in the market and Table 1 shows the nominal composition of the four most well known, It can be seen that S32750 has no additions of tungsten or copper, while S32550 contains only copper and S39274 contains only tungsten. Zeron 100 (S32760) contains additions of both tungsten and copper. However the level of these additions varies considerably from alloy to alloy, particularly tungsten. The presence of these additions has no significant effect on mechanical properties, and all four alloys are supplied to similar minimum properties i.e.:

0.2% Proof Stress	-	550 MPa
UTS	-	750 MPa
Elongation	-	25%
Hardness	-	28 HRC Max.

## 3.0 METALLURGY

### 3.1 Alloy Composition

The super duplex stainless steels were a development of the early 25%Cr duplex alloys, such as Zeron 25. The aim was to produce an alloy with improved mechanical properties and with increased corrosion resistance in oxidising chloride solutions, such as sea water. The elements which contribute to corrosion resistance in such environments are chromium, molybdenum and nitrogen. They are often linked by the Pitting Resistance Equivalent Number or PREN,

$$\text{where PREN} = \% \text{ Cr} + 3.3\% \text{ Mo} + 16\% \text{ N}$$

This is an empirical equation which gives an indication of the resistance to localised attack in the presence of chlorides.

Early 25%Cr duplex alloys had PREN values of 35 to 38, while the superduplex alloys have a PREN in excess of 40. When adding increased levels of chromium and molybdenum it is important to balance the alloy properties so that not only is the required corrosion resistance achieved, but also the mechanical properties, phase balance, freedom from precipitates etc. The effects of molybdenum and nitrogen can be modified



by small additions of other elements to achieve a balanced composition. The composition of Zeron 100 was derived in 1985 and has remained fixed since that time.

### 3.2 Precipitation of Sigma

When duplex stainless steels are heated above 300°C precipitates of third phases will form after a while. In the temperature range 300° to 600°C the principal precipitate is alpha prime, while in the range 700° to 1000°C the principal precipitates are sigma and chi. This is shown in the time temperature transformation (TTT) curve in Figure 1. From the TTT curve it can be seen that sigma will precipitate at much shorter times than alpha prime and, hence, there is more concern about sigma precipitation.

Sigma is an intermetallic phase enriched in chromium and molybdenum which precipitates from the ferrite phase. When it forms it leaves a denuded matrix around the precipitate which is more susceptible to corrosion. The presence of sigma also greatly reduces ductility, giving low impact toughness energies. Hence sigma is extremely detrimental, and is avoided in wrought and cast products after hot working by annealing at temperatures above the sigma 'nose' i.e. >1100°C, to homogenise the alloy, followed by water quenching. It is also important to quench to below 300°C to ensure no precipitation of alpha prime.

In addition to the manufacturing process, there is concern over the production of sigma during the heating, and re-heating, associated with welding operations, and some of the alloying elements in superduplex stainless steels contribute strongly to the sensitivity to sigma precipitation.

Chromium molybdenum and tungsten are all known to increase the sensitivity to precipitation (2) i.e. move the 'nose' of the TTT curve to the left. Molybdenum and tungsten also tend to extend the sigma envelope to higher temperatures (2). However, the relative contribution of the elements is not equal, and some have a greater propensity than others to increase the likelihood of precipitation. Hull (3) devised an equation for sigma susceptibility based on the chromium equivalence of each element.

$$\begin{aligned} \text{Cr equiv} &= \text{Cr} + 0.31 \text{ Mn} + 1.76 \text{ Mo} + 0.97 \text{ W} + 2.02 \text{ V} \\ &+ 1.58 \text{ Si} + 2.44 \text{ Ti} + 1.70 \text{ Nb} + 1.22 \text{ Ta} \\ &- 0.226 \text{ Ni} - 0.177 \text{ Co}. \end{aligned}$$

This equation shows that molybdenum and tungsten both increase the tendency to sigma formation, but the influence of tungsten is only 0.55 that of molybdenum and is slightly less than that of chromium.

Some calculations for typical heats of some superduplex stainless steels gave the following results:-

Zeron 100 Cr. Equiv	=	30.3
S32750 Cr Equiv.	=	30.7
S39274 Cr Equiv.	=	31.7

The slightly greater value for S32750 compared with Zeron 100 is due to the higher molybdenum content of the S32750 alloy. The much greater chromium equivalent for S39274 is because although the alloy has a slightly lower molybdenum content compared with the other two alloys, it has a high tungsten content. These values suggest that



sigma precipitation should be least likely in Zeron 100, with S32750 slightly worse and S39274 much worse.

The equation of Hull takes no account of carbon or nitrogen, but as the levels of the former are very low in all three alloys and nitrogen contents are very similar, this would not greatly affect the relative chromium equivalent ranking.

Hertzmann et al (4) carried out tests on welds of superduplex alloys. These were all produced by manual metal arc welding with over-alloyed consumables (~9% Ni) to ensure the correct microstructure in the as-welded condition. These welds were produced with normal heat inputs for 20mm plate i.e. 0.8KJ/mm or 1.4KJ/mm. Hertzmann et al carried out short ageing tests (0 to 90s) at 850°C, 900°C and 950°C to simulate excessive heat inputs and they determined the production of precipitates by measuring the impact toughness. Figure 2 shows typical results after ageing at 950°C. The results at 850°C and 900°C were similar.

The results show that even 10s of heating produced a loss of toughness of S39274. Zeron 100 and S32750 maintained toughness after 10s and showed a gradual decrease in toughness at longer ageing times. The results were supported by microstructural examinations showing that precipitates form very quickly in alloy S39274. There were no significant differences between Zeron 100 and S32750.

Huhtala et al (5) constructed continuous cooling transformation (CCT) curves for welds in alloys S39274, S32750 and S32760, as shown in Figure 3. It can be seen that the time to precipitate sigma is much shorter for S39274 compared with the other alloys.

S39274	=	55 secs
S32750	=	162 secs
S32760	=	135 secs

This shows a greater propensity to sigma formation in welds of the high tungsten alloy. The work of Huhtala et al used S32760 which is the UNS number to which Zeron 100 is also made. However, Huhtala's alloy contained 0.9 wt % tungsten while Zeron 100 normally contains 0.6 to 0.7 wt % tungsten. From the data presented by Huhtala it is expected that Zeron 100 would show a virtually identical CCT curve to the S32750 alloy.

Jana (6) investigated welds of superduplex stainless steel made with different filler metals containing various concentrations of copper and/or tungsten. The weld quality was assessed by metallography and the critical pitting temperature in ferric chloride solution. Jana found a lower CPT for filler metals containing only copper, but copper had no effect when tungsten was also present. The CPT increased as the tungsten increased, up to 2% tungsten. Tungsten retarded the formation of inter metallic precipitates and secondary austenite. This work shows that the benefits of tungsten for corrosion resistance in the parent metal are also conferred to the welds. The results of Jana contradict those of Huhtala. Although there is disagreement about the effects of 2% tungsten additions, all the results show no significant deleterious effects with 0.7% tungsten.

The conflicting results for the effect of individual elements are not as important as the overall metallurgical balance. The corrosion resistance is governed not only by tungsten, but also by chromium, molybdenum and nitrogen,

---

$$\text{i.e. PREN} = \% \text{Cr} + 3.3 (\% \text{Mo} + \% \text{W}/2) + 16x\% \text{N}$$



The phase balance is equally important i.e. the greater the austenite content the more enriched the ferrite becomes due to segregation and the greater the PREN of the ferrite compared with that of the austenite. Hence, small changes of composition and/or phase balance can dramatically change the results in tests like those of Huhtala (5) and Jana (6). Zeron 100 has always been manufactured with a closely controlled composition to ensure optimum phase balance and element partitioning.

### 3.3 Fabrication Experience

Zeron 100 has been used extensively in the North Sea, North & South America, the Middle East, the Far East and Alaska for seawater and process piping, Table 2 lists some of the projects supplied by RA Materials. There have been very few fabrication problems with these projects which have covered a whole range of sizes from 3mm wall to 62mm wall thickness.

Mohagen (7) describes the fabrication experience with Zeron 100 on the Embla project. Techniques were devised to produce welds with the required properties and no problems were experienced with precipitates.

Bowden (8) describes the experiences of Marathon in qualifying thin-walled, small diameter superduplex pipe for the East Brae project, (eg. 2" Sched 10s). Precipitates were observed in the HAZ of the welds independent of alloy choice. Test welds were made in alloys S32550, S32750 and Zeron 100 and all the alloys produced some precipitates on welding thin walled pipe (<1%). A fitness for purpose evaluation showed that the levels of toughness being obtained were adequate for the project.

As superduplex alloys have more alloying additions than other duplex stainless steels there is more risk of precipitates forming during welding. This is most predominant in thin walled tubing, as the cooling rates which are achievable are reduced due to the reduced mass, giving a much reduced welding envelope.

J. R. Still (9) reported a similar problem to Bowden on another North Sea installation. This was also overcome by demonstrating fitness for purpose with low levels of precipitates (up to 2.5% sigma).

Zeron 100 was the first superduplex stainless steel and it is the alloy that has been used in most of the offshore applications of superduplex for both seawater and process applications. Hence there is far more experience with Zeron 100 than with S32750 and S32550. There has only been limited use of S39274 in the North Sea.

The whole fabrication experience with Zeron 100 shows that welding of Zeron 100 can be carried out without undue precipitate formation even in severe cases, and welding of Zeron 100 presents no more problems than other superduplex alloys. Alloy S39274 was not available when the Marathon evaluations were carried out and so it is not known whether it would have performed similarly to the other alloys. However, the work of Hertzman and Jana suggest it could be worse.

#### 4.0 CORROSION

There have been a few studies specifically aimed at the effects of tungsten on corrosion. Nagano et al (10) showed that tungsten increases the immunity potential of duplex stainless steels to crevice corrosion.

Okamoto (11) carried out a range of corrosion tests on a 25%Cr duplex stainless steel with levels of tungsten from 0.2 to 4.0 wt %. He showed that the resistance to localised corrosion increased with increasing tungsten content in a range of tests including the ASTM G48A and electrochemical tests in both oxidising and reducing chloride solutions.

The relative contribution of alloying elements to localised corrosion resistance is often assessed by the pitting resistance equivalent number (PREN)

where:  $PREN = \% Cr + 3.3 \times \% Mo + 16 \times \% N$

Okamoto (11) showed that the beneficial effect of tungsten was about half that of molybdenum and can be accommodated in the formula as follows:

$$PREW = \% Cr + 3.3 (\% Mo + 0.5 \times \% W) + 16 \times \% N$$

The table below shows the typical PREN and PREW values for all the common super duplex alloys.

ALLOY	PREN	PREW
S32550	41.7	41.7
S32750	41.9	41.9
ZERON 100	40.8	41.8
S39274	39.1	42.4

It can be seen that the inclusion of tungsten in the PRE equation brings the pitting resistance equivalents of all four alloys roughly into line. Zeron 100 is the only alloy that guarantees a minimum PREN within its specification of greater than 40.

#### 4.1 Seawater

Both Zeron 100 and S32750 have been used extensively in seawater systems with no corrosion problems reported. Laboratory tests carried out by Sintef (12, 13) showed that the performance of S32750 and Zeron 100 was similar with good resistance to pitting at welds and in flange crevices in warm, chlorinated sea water.

In seawater cooling systems the temperature in discharge pipework can sometimes be subject to short or long upsets when increased fluid cooling is required. The effect of such process upsets on a 6%Mo austenitic alloy (S31254) and S32750 super duplex was studied by Valen et al (14).

They found that crevice corrosion readily initiated on both alloys at 70°C and repassivation on cooling never occurred above 20°C, and only at 10°C on some specimens. Tests by Francis et al (15) on Zeron 100 and S31254 found that crevice corrosion initiated on all the 6%Mo samples at 70°C and repassivation occurred at around

25°C, although in some cases the crevice was so large it had opened out, permitting loss of the acidic crevice fluids. Only half of the Zeron 100 specimens initiated attack and of those that did, all had repassivated by the time the temperature dropped to 42°C. The good performance of Zeron 100 was ascribed to its good resistance to the acidic, chloride environment in the pit, due to its content of tungsten and copper. Service experience supports the findings of the laboratory tests (15, 16).

#### 4.2 Oil and Gas Process Fluids

The use of alloys in sour oil and gas fluids is defined by the ISO15156/NACE MR0175. The H<sub>2</sub>S limit for all superduplex stainless steels (PREW>40) is 0.2 bar (20kPa; 3psi) is 3 psi (0.2 bar) H<sub>2</sub>S. There is no detailed data published on the sour limits for S32750, but extensive laboratory testing has shown that Zeron 100 can tolerate levels of H<sub>2</sub>S much greater than 0.2 bar if the pH is > 4 or if the chlorides are < 120,000 mg/l. In one test Zeron 100 showed no signs of cracking at 90°C with 1 bar (15 psi) H<sub>2</sub>S with 15,000 mg/l chloride at a pH of 4.8 (at temperature and pressure). Zeron 100 is in service in several fields at H<sub>2</sub>S levels exceeding the 0.2 bar limit in ISO 15156/MR0175.

Barteri et al (17) examined the sulphide stress corrosion cracking limits of cold worked 25%Cr duplex stainless steel, both with and without tungsten. The tungsten addition was only 0.3 wt % but the data, obtained from slow strain rate testing, showed a clear advantage for the heavily cold worked alloy with tungsten (Fig 4). It appears that the composition of Zeron 100 has optimised the tungsten content for resistance to cracking in sour brines.

#### 4.3 Chemical Environments

Superduplex stainless steels are being increasingly used by the chemical industry because of their excellent resistance to chlorides at high temperatures. However, these alloys also have good resistance to some of the commonly used acids. Figure 5 shows the iso-corrosion curves (0.1mm/y) for S32750 and Zeron 100 in sulphuric acid. Alloy 316L is included for comparison. No data for S39274 has yet been published.

It is well known that copper contributes to the good performance of stainless steels in sulphuric acid but tungsten is also thought to contribute. The mechanism by which these additions confer corrosion resistance in non-oxidising acids is not known. A similar advantage is seen in sulphuric acid containing chlorides (18).

Figure 6 shows the iso-corrosion curves for S32750 and Zeron 100 in hydrochloric acid. Again, the superior resistance of Zeron 100 is thought to be due to its copper and tungsten content.

A similar relationship exists in other non-oxidising acids such as phosphoric acid; hence the presence of tungsten in Zeron 100 gives it superior resistance to corrosion compared with S32750 in common non-oxidising acids.

## 5.0 CONCLUSIONS

1. While high levels of tungsten (~2%) may increase the susceptibility to sigma formation in duplex stainless steel welds, there is no significant difference between Zeron 100 and a similar tungsten-free alloy. This is borne out by service fabrication experience.

2. Tungsten contributes to resistance to localised attack in oxidising chloride solutions and no difference between Zeron 100 and a tungsten free alloy has been seen in a range of test media, including chlorinated seawater.
3. The level of tungsten in Zeron 100 (0.5 to 1.0 wt %) appears to give optimum resistance to sulphide stress corrosion cracking in sour brines.
4. The joint additions of tungsten and copper give Zeron 100 excellent resistance to sulphuric and hydrochloric acids, superior to that of alloys which do not have these additions.
5. The properties of a superduplex alloy require a correct balance of composition to give optimum mechanical properties, corrosion resistance, phase balance, freedom from precipitates etc. The composition of Zeron 100 combines the additions of molybdenum, tungsten, nitrogen and copper to give the optimum values of all these properties.

## REFERENCES

1. C V Roscoe and K J Gradwell, Paper 34, Duplex Stainless Steels, The Hague, Holland, October 1986.
2. J Charles, Duplex Stainless Steels '91, Beaune, France, October 1991, Les editions de physique, P.3.
3. F C Hull, Welding Research Supplement, March 1973, P104S.
4. S Hertzman, M Nilsson & R Jargelius-Pettersson, Paper 1, 4<sup>th</sup> International Conference on Duplex Stainless Steels, TWI, Glasgow, Scotland, November 1994.
5. T Huhtala, J-O Nilsson, A Wilson & P Jonsson, Paper 43, *ibid*.
6. S R Jana Duplex Stainless Steels '97 Maastricht, Holland . Oct 1997 KCI Page 939.
7. S Mohagen, Manufacturing/Fabrication Experience with 25 Cr Duplex Steel Corrosion and Materials Offshore; conference organised by NITO, Oslo, Norway, September 1994.
8. P Bowden, Experiences in Welding 25 Cr Super Duplex Stainless Steel for Topsides Hydrocarbon Piping: *ibid*.
9. J R Still, Welding and Metal Fabrication, August/September 1994, Page.331.
10. H. Nagano, T. Kudo, Y Inaba & M. Harada, *Metaux Corrosion Industrie* No.6678, P.23.1, 1981.
11. H. Okamoto, Application of Stainless Steel '92, Stockholm, Sweden, June 1992, Vol .1, P.360.
12. J M Drugli, U Steinsmo, P O Gartland and T Rogne, Paper 645, Corrosion '93 NACE, New Orleans, USA, March 1993.



13. P O Gartland, U Steinsmo & J Drugli, Paper 646, *ibid.*
14. S Valen, P O Gartland & U Steinsmo, Paper 496, *ibid.*
15. R Francis, J B Irwin & G Byrne, *Brit. Corr. J.* 30 (1995) 237.
16. R. Francis and G. Byrne, "Experiences with Superduplex Stainless Steel in Seawater", *Stainless Steel World*, Vol 16, June 2004, page 53, KCI
17. Barteri, G Rondelli, L Scoppio & A Tamba, *Duplex Stainless Steels '91*, Baune, France, October 1991, P.1203, Les editions de physique.
18. R. Francis, G. Byrne and G. Warburton  
Nickel-Cobalt '97. 36<sup>th</sup> Annual Conference of Metallurgists of CIM,  
Sudbury, Ontario, Canada – August 1997. Vol IV page 25



TABLE 1 Nominal composition of some commonly used superduplex stainless steels

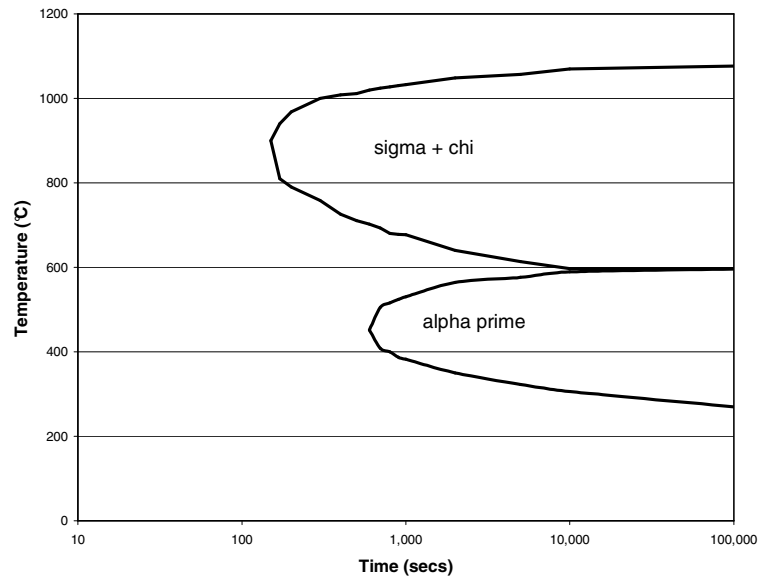
UNS No.	Common Name	Nominal Composition (wt %)						
		Fe	Cr	Mo	Ni	N	Cu	W
S32760	Zeron 100	Bal	25	3.5	7	0.25	0.7	0.7
S32750	SAF2507	Bal	25	3.8	7	0.27	-	-
S32550	UR 52N +	Bal	25	3.8	6	0.26	1.5	-
S39274	DP3W	Bal	25	3	7	0.26	-	2



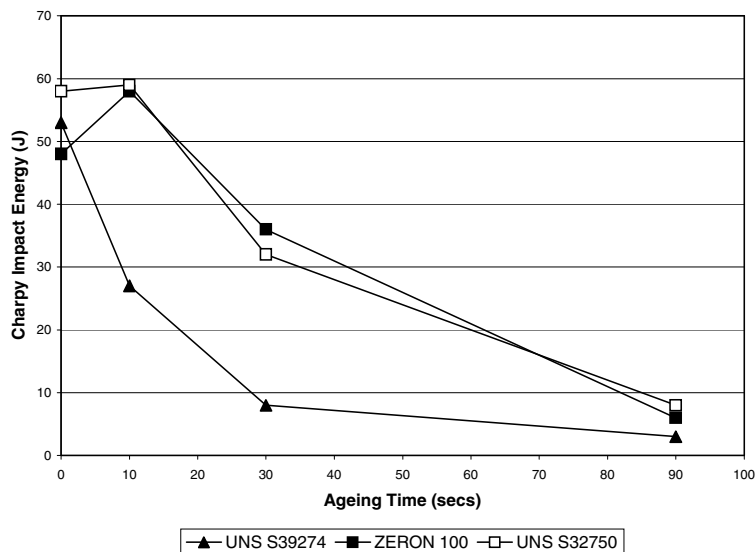
**TABLE 2     Some projects which have utilised Zeron 100 Superduplex Stainless Steel**

<b>PROJECT</b>	<b>COMPANY</b>	<b>ITEMS</b>
Ivanhoe/Robroy	Amerada Hess	Sea Water System
Veslefrikk	Statoil	Process Pipework
Beryl A	Mobil	Firewater/Deluge
Claymore	Occidental	Flowline
West Sole	BP	Flowline
Morecambe Bay	British Gas	Sea Water Discharge
Piper Bravo	Elf Enterprise	Process Pipework
East Brae	Marathon	Process Pipework
Goodwin	Woodside	Sea Water System
Bruce	BP	Sea Water System
Scott	Amerada Hess	Process Pipework
Embla	Phillips	Process Pipework
Scott	Amerada Hess	Sea Water System
Prudoe Bay	Arco	Flowlines
Liverpool Bay	Hamilton/BHP	Sea Water System

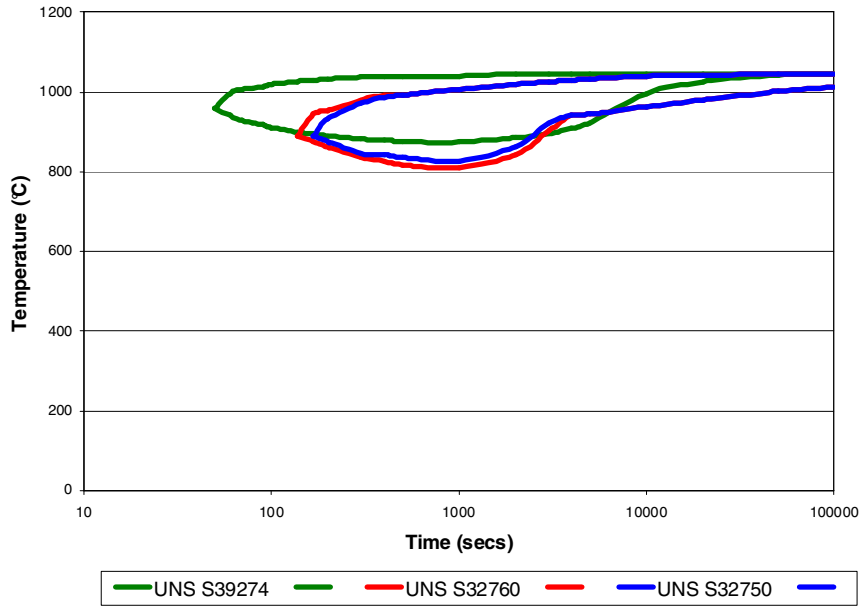
**Figure 1 Typical TTT curve for a super duplex stainless steel (Ref 2)**



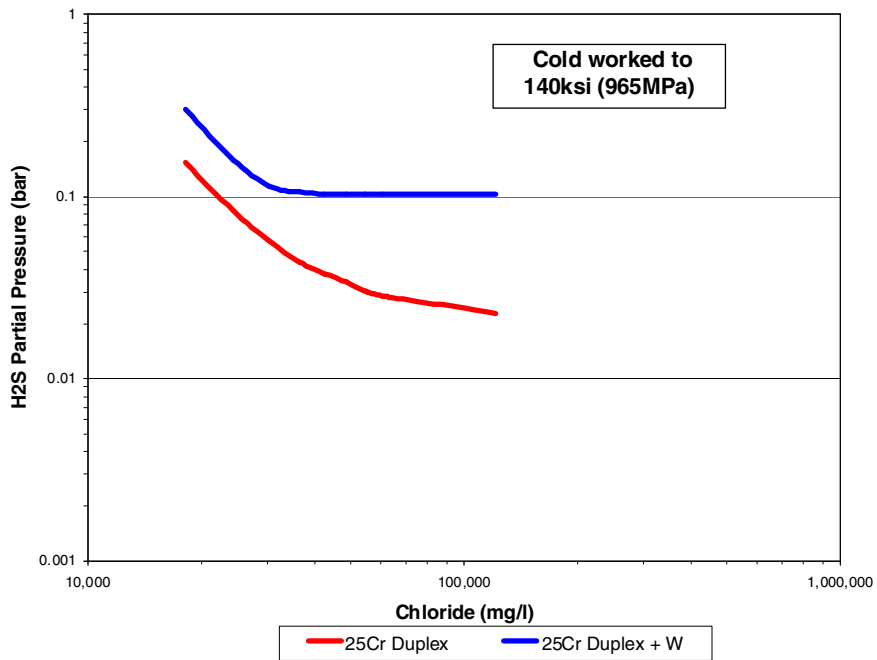
**Figure 2 Charpy impact energy after ageing at 950°C for three super duplex stainless steel welds**



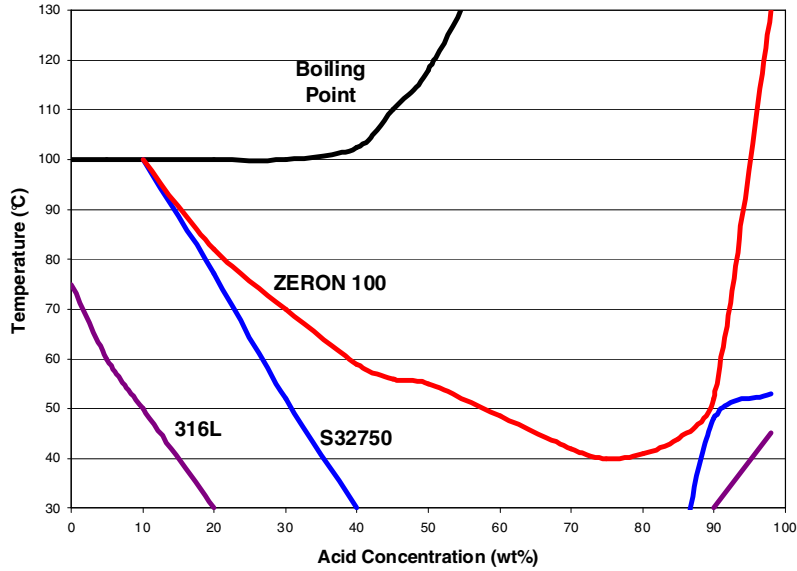
**Figure 3 CCT diagram for three super duplex stainless steels for 1% sigma (Ref 4)**



**Figure 4 Sulphide SCC limits by SSRT for 25Cr duplex stainless steels (Ref 16)**



**Figure 5 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid**



**Figure 6 Iso-corrosion curves (0.1mm/y) for some stainless steels in hydrochloric acid**

