Corrosion Management of Assets Constructed in Super Duplex Stainless Steels Topside and Subsea - A Suppliers Perspective

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ABSTRACT

Super Duplex Stainless Steels (SDSS) are utilised extensively by the oil and gas industry offshore, on fixed platforms, production vessels and subsea developments because they provide an excellent combination of;

a) Strength, weldability, fracture toughness and structural integrity.
b) Corrosion resistance in natural and chlorinated seawater.
c) Corrosion resistance in CO_2/ H_2S/Cl^- process environments.
d) Corrosion resistance in in marine atmospheres.
e) They have high design strength, allowing weight savings through the construction of lower wall thickness, pipe work systems, process equipment and vessels.
f) They are readily available in all cast and wrought product forms.
g) They provide long life/minimum maintenance functionality to facilities that means that they are not normally manned and personnel are not exposed to the arduous offshore conditions.
h) They provide lower level, cumulative, through life costs when compared with alternative material selection philosophies.

As such they find application in seawater cooling and fire protection systems, topside and subsea production pipe work, flow lines and pipelines. However, this presupposes that all items in the bill of materials are consistently and repeatedly properly processed, heat treated, pickled and passivated, fabricated, installed, commissioned, operated, maintained and deployed in environments within the limits of their application range. With over 30 years of wide scale use of these alloys by the oil and gas industry the overall experience has been good. However, intermittently problems recur. Some, like intermetallic precipitates in products are high profile and well known, but others are less well known. Based on alloy development and manufacturer independent supply experience of super duplex steel over a 30 year period the paper considers some of the less well known but recurring problems and the methods used to ameliorate them. From this information it is hoped that corrosion management strategies can be enhanced to sustain and or extended practical limits of use of this grade of steel in the future.

Key words: Duplex Stainless Steel; Forging; Toughness; HISC, Welding, Sigma, Crevice Corrosion,

INTRODUCTION

Over the years we have seen a number of corrosion problems where asset integrity management has either repeatedly omitted to address fully certain issues or simply read across from previous project work flawed engineering design concepts. This has resulted in a number of issues that can now be considered "common themes" for SDSS. These can be categorized as follows

- a) Exceeding design conditions (start up, steady state, operational transients, shutdowns)
- b) Problems with special case items
- c) Poor supply chain knowledge and subcontracting and capability to procure properly.
- d) Quality of the material of construction
- e) Quality of fabrication

We now consider some of these less well known "common theme" issues, as they relate to project experience in seawater and process pipe work applications. We also provide additional information that can be used by the engineering contractor to prevent problems and or improve performance of these grades. This is supported with a combination of anecdotal field experience and the results of corrosion tests to establish safe working ranges for these alloys and to understand if they can be extended.

Experimental Procedures

Materials Used.

12.5mm dia. ZERON(†) 100 (Z100, UNS S32760) bar was machined in to 10mm diameter crevice corrosion test "bullets". These were ground to 1200 grit finish using SiC paper and passivated in air for at least 24 hours before testing. Each was screwed to a brass rod, for electrical connection, mounted through a glass rod, with a PTFE seal between the glass and the specimen, as shown in Figure 1a. Specimens were coated with lacquer on the end face. A silicone rubber O-ring seal of square section, with an id of 7mm and a width of 4mm was placed around the diameter of bullet to form the crevice before testing. To establish the Critical Pitting Temperature (CPT) of welds, two 500 x 150mm x 4mm thick Z100 plates with a Vee preparation on the long side were joined by Tungsten Inert Gas (TIG) welding using Z100X grade welding consumables. All the welds were thoroughly wire brushed with a stainless steel brush. Micro-sections of the weld showed a two-phase structure in the weld, with ferrite contents in the range 50% to 60%. A small quantity (less than 1% volume fraction) of sigma phase was seen in the Low Temperature Heat Affected Zone (LTHAZ) of the welds. This was as an array of very fine, isolated, precipitates (approximately 1 to 2µm in diameter) that were evenly dispersed at ferrite/austenite grain boundaries, growing in to the ferrite phase. This is typical of the LTHAZ of thin wall SDSS welds. The pitting corrosion test samples cut out of the welded plate were 60mm x 12mm x 4mm with the welds across the centre. The cut edges were ground to 240 grit using SiC paper, and the sharp edges were bevelled. A 250mm length of welding wire was tack welded to one of the short edges for an electrical connection. The tack weld and the lower portion of the wire were coated in lacquer to prevent their wetting by seawater, as shown schematically in Figure 1b.

Evaluation of the Critical Pitting Temperature (CPT) and the Relative Critical Crevice Temperature (RCCT) in Seawater Solution at Different Potentials.

Crevice corrosion test samples were subjected to potentiostatic electrochemical testing in glass vessels of capacity 750ml. These were filled with synthetic seawater with pH 7.8 – 8.2 (adjusted with NaOH) made as follows:

NaCl	-	28g/l
$MgSO_4 . 9H_2O$	-	7.74g/l
$MgCl_2 . 6H_2O$	-	6.02g/l
$CaCl_2 . 6H_2O$	-	2.27g/l
$NaHCO_3$	-	0.2g/l

(†) Trade Name

Compressed air was continuously bubbled through the seawater and the specimens were mounted so that the water line was ~10 mm below the upper sample edge. This meant that the weld deposit, both HAZ's and some parent metal were immersed. The total surface area under water was ~14cm^2 for the welded samples and ~9cm^2 for the parent metal "bullets". After sample immersion, the potential was allowed to stabilise for about 15 minutes. The samples were then gradually polarised to the set potential over 30 minutes. The current was then allowed to stabilise for one to two hours at room temperature, after which the temperature was increased at ~ 5°C/hour up to ~ 90°C where it was allowed to remain for two hours. The current and temperature were monitored continuously throughout the test. The CPT and RCCT were taken as the temperature when the current density exceeded 10µA/cm^2. After testing, the samples were washed, dried and examined under a microscope for indications of corrosion. The term "relative" CCT is used because the result obtained is relative to the o ring seal crevice former used in the test.

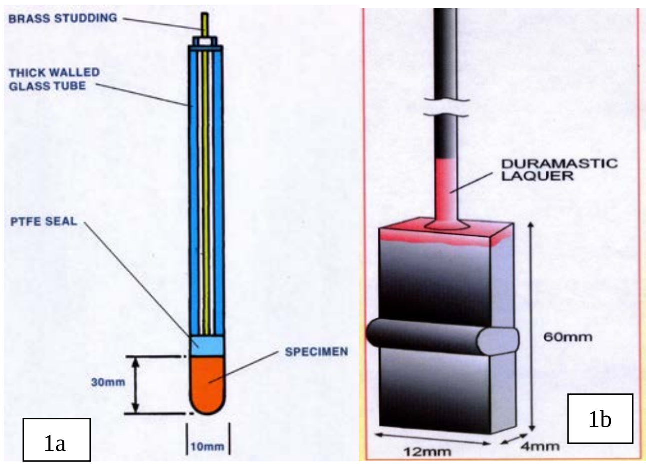


Figure 1: a) Schematic Diagram of the Assembly Used to Measure RCCT (Silicone O Ring Seal Omitted for Clarity) and b) Schematic Diagram of Welded Sample Used to Measure CPT.

Assessment of the Resistance to Hydrogen Induced Stress Cracking (HISC) as a Consequence of Cathodic protection (CP).

Tensile test samples were taken from 150mm NB XXS seamless pipe, 130.175mm 10k forged weld neck flanges, 12.5mm, 114.3mm and 160mm diameter bars in generic super duplex stainless steel grade UNS S 32760 and Z100. Samples were also taken from 130.175mm 10k forged weld neck flanges made in the grade Z100 AFP[(†)] (Advanced Forged Product). This is a product with modified and controlled chemistry, forging and heat treatment practice applied. We will refer to this grade as Z100 modified. These samples were loaded in to a glass chamber and immersed in 750ml of synthetic seawater solution as detailed above. The samples were then polarized to a potential of - 1.0 to – 1.1 V (SCE). They were stressed in a Slow Strain Rate Testing (SSRT) machine at a strain rate of 1x 10^{-3}/s up to various percentage levels of their actual 0.2% proof stress. These samples were then held at a constant load for 720 hours. They were then examined by liquid penetrant testing and metallography for cracking.

Common Themes

Crevice Corrosion of Flange Faces and Threaded Connections in Chlorinated Seawater.

In the late 1980's the design case for seawater cooling systems built in SDSS (and super austenitic steels (SASS)) was a maximum temperature of 40ºC, based on a residual chlorine content of 0.8ppm[1]. Since this time this temperature limit has been revised to as low as 15ºC and then increased to 20ºC, this being driven by North Sea experience[2]. However, there are a number of issues driving these changes. Crevice corrosion of flange faces was one. During commissioning operators were having difficulty keeping within safe chlorination and temperature limits[2-6]. Improved instrumentation and control systems now mean that chlorination levels are better controlled but temperature excursions do happen during start up and for operational reasons during production. Shone et al[1], demonstrated how potential of stainless steel in seawater changed with chlorination level (Figure 2).

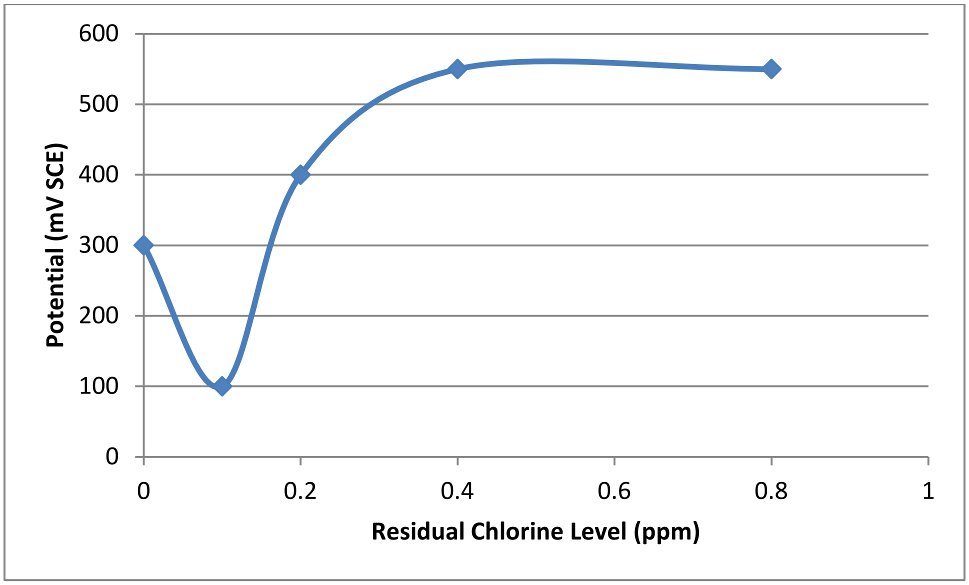


Figure 2: the Relationship between the Potential of SDSS in Seawater and Residual Chlorine level

In natural, aerated seawater the potential of stainless steels is usually +300 to +350mV (SCE). In chlorinated seawater (0.5 to 0.8ppm residual chlorine after disinfection) the alloy would typically have a potential of +500 to +600mV (SCE). When de-aerated to say 200ppb the potential is about +100mV (SCE). Crevice corrosion testing, as described above, was used to measure RCCT over a range of potentials of interest to the oil industry. As you can see from Figure 3, this means the RCCT can range significantly, especially at lower potentials. Typically, residual chlorine design levels in sea water systems do not exceed 0.7ppm (quite oxidizing levels (around +600mV(SCE)), but from Figure 2, about 0.1ppm residual chlorine gives a potential of about +100mV (SCE). This level of residual chlorination is known to effectively disinfect and if it can be practically maintained in seawater systems then levels of RCCT can be increased by as much as +30ºC. It should be noted that previous work identified that the results of RCCT testing using this crevice former correlated well with service experience of flanges in sea water service up to 40ºC with neoprene gaskets[7]. So, controlled low level chlorine dosing at the 0.1 ppm level could provide a useful tolerance for process upsets in temperature during commissioning.
In other problem cases, heat trace cabling installed to avoid freezing pipes, made them so hot that they initiating crevice corrosion at flange faces and pitting in the high temperature HAZ of welds[2]. On other occasions design temperature limits were exceeded for dewaxing and other operational reasons[5]. This experience highlighted two factors that were not previously considered in the seawater application of these grades. Firstly, it was found that Cu and W bearing SDSS grades had much better re-passivation characteristics than those SDSS and SASS without these additions[7]. This means that the Cu and W bearing grades can experience short periods of process upsets that initiate corrosion attack, but when normal operating conditions are resumed the passive film is reformed and the corrosion attack no longer continues to propagate. This is because their re-passivation temperature is higher than the normal operating temperature. So, they can be more tolerant to process upsets than the other SDSS and SASS grades where corrosion attack would continue to propagate under normal operating temperatures and below[8]. In contrast to the above, one project[5,7] ran with temperatures up to 65ºC for prolonged periods of time, as the heat exchangers were found to be far more efficient than expected.

However, the wide spread corrosion damage that was anticipate never materialized. This was believed to be due to the fact that the project had run cold, chlorinated seawater through the cooling system for several months before becoming operational. This process appears to enhance the quality of the passive film within the entire system and coax from the system a higher inherent resistance to corrosion attack. This experience led to the proposal that operators adopt a so called "soft start up" for seawater systems, running cold chlorinated seawater for a short period before producing[9, 10].

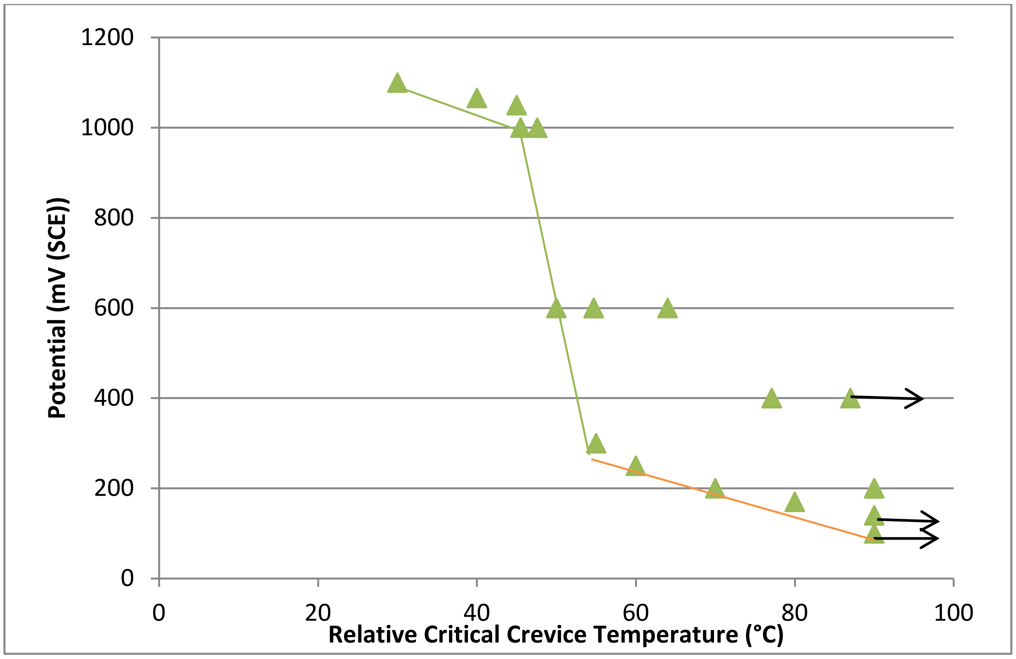


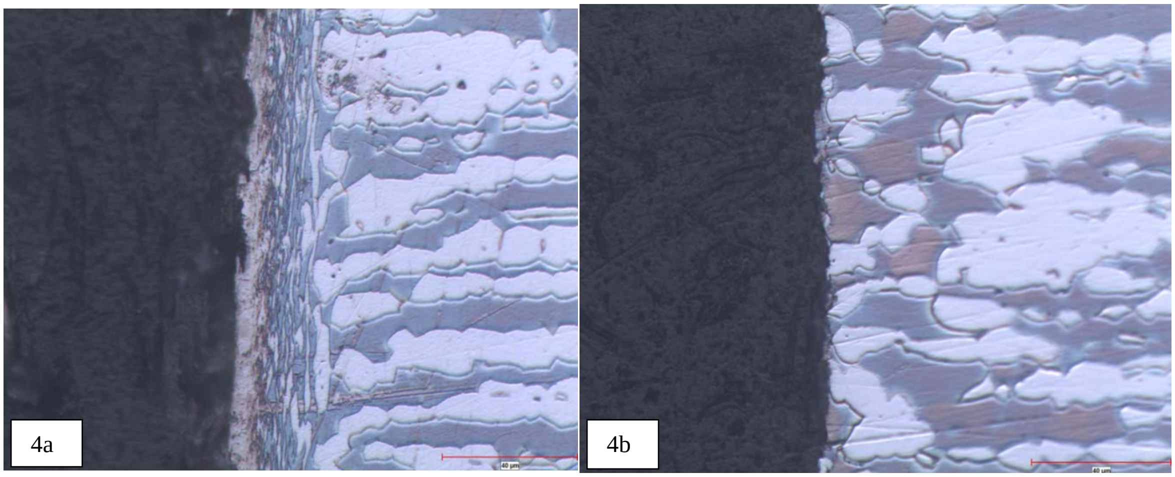
Figure 3: the Effect of Potential on RCCT for Z100 Parent Material in Seawater Solution

Recently US Navy work[11] has identified the effect a soft start up has on the chemistry of the passive film, concluding that it reduced both the degree of hydration and the chloride content of the passive film. This means that the performance of pipe work systems is influenced by how it is introduced in to seawater service. It is best to run the system cold and chlorinate gradually before heating. The worst case is to start up using warn, chlorinated seawater.

Other crevice corrosion problems have occurred because of galvanic corrosion. In 1990 the use of Nickel Aluminum Bronze (NAB) castings for valve bodies and sea water sprinkler head nozzles in SDSS pipe work systems has proved very problematical[12]. Not only did the flange faces of the NAB valves corrode but the corrosion product in the crevice then became so aggressive due to hydrolysis that the SDSS joining flange faces also suffered attack. Sometime after the event it was realised that the copper alloy corrosion products then deposited within the pipe work system influenced the on going corrosion resistance of the system adversely[13]. Copper deposits were found to increase the efficiency of the cathodic reaction, increasing current density measurements by 2 orders of magnitude. This could explain the ongoing corrosion problems that were experiences for several more years.

The use of graphite loaded gaskets and spiral wound gaskets with 316 (UNS S31603) or alloy 400 (UNS NO4400) windings can also be a problem[14] if the graphite becomes exposed to seawater. In this case it behaves as a highly efficient cathode and drives the kinetics of the initiation and propagation of crevice corrosion and as such should be avoided. While this is now well known some projects have used graphite filled gaskets despite engineering instructions not to do so[2]. In the case of the 316 and alloy 400 spiral windings these grades simply lack the necessary crevice corrosion resistance and their corrosion products can cause attack of the flange material[15]. It is also now clear that PTFE[(†)] as a gasket material constitutes quite a crevice corrosion risk and are best avoided[16]. Aramid[(†)] gaskets for example give higher crevice corrosion initiation temperatures when tested in like for like crevice test assemblies.

The crevice corrosion resistance of threaded connections has also been cited as a reason why allowable operational temperatures have been kept so low by some operators. However, close examination of the method of manufacture of threaded connections and crevice corrosion tests (similar to those described above but using nuts and threaded bar test assemblies) has shown that the removal of deformed surface layer of cut threads can increase the crevice corrosion resistance of these parts by as much as 15ºC (Figure 4). This benefit is not, as yet widely known. Although the additional processing does incur a small cost increment the, the avoidance of crevice corrosion of threaded connections is a significant enhancement.



RCCT (°C)	
"As Received"	"Acid Softened and Pickled"
61.7	75.6
65.8	79.8

Figure 4: RCCT of Machined threads a) As Received b) chemically treated and pickled

Pitting Corrosion of Welds in Seawater

The corrosion resistance of welded joints in seawater applications, especially 6"NB sch. 40s and below has also been a longstanding issue. The experience of two West Australian projects, dating back to the early 1990's, has been principle in driving this issue[12]. There were several factors that fall in to our group of common themes that account for the poor performance of these projects. Some of the batches of smaller sizes of seamless pipes had intermittently been subject to a slack quench from heat treatment temperature during manufacture. The quench was sufficiently fast to avoid precipitation of intermetallic phases in the pipes (so no intermetallic's were seen in the microstructure as delivered) but it was also sufficiently slow to use up all the incubation time it takes for intermetallic phases to precipitate. This meant that when subjected to a further thermal cycle from welding, the fabricator could not avoid intermetalic formation in LTHAZ of the joint as this region coincided with the 850ºC to 900ºC temperature range where intermetallics precipitate most readily. Because the slack quenching was intermittent the issue never presented itself during weld procedure or welder qualification. It took some time to understand this problem, but when resolved the Welding Institute[(†)](TWI) suggested that the welding restrictions that had been applied to these alloys as a consequence of these problems were overly severe and could be relaxed[17]. Also, it was later realized that pipe wall temperatures up to 65ºC were being experienced in pipes exposed to direct sunlight. This compares with a design case of 45ºC maximum [18]. Generally, control of heat input, inter-pass temperature, the use of stringer beads, the correct shielding and backing gasses, balanced or quadrant welding and the "cold pass" technique provides high integrity welds in thin wall pipe work systems[19]. Attention to detail during weld procedure and welder qualification pays dividends, particularly if welds inside and outside acceptable parameters are made and tested. Corrosion test samples can be a very graphic visual aid in emphasizing to welders the importance of keeping within the qualified welding parameters. Corrosion attack of welds can occur in the weld metal and LTHAZ regions (Figure 5a and 5b). It is possible to form intermetallic phases in both the weld deposit (Figure 6a) and LTHAZ (Figure 6b) regions. These reduce both toughness and corrosion resistance but a certain amount of tolerance to the precipitate is available. Generally, corrosion resistance of weldments can be retained with as much as 4 or 5% inter metallic in thin wall joints[20] and adequate toughness retained in thick joints with as much as 2.5% of inter metallic phase being present[21, 22]. This is because the morphology of the intermetallic phases formed as a consequence of the steep temperature gradients of the weld thermal cycle are very different to those formed isothermally during heat treatment processes. It tends to form as smaller, irregular particles, more dispersed, less interconnected than isothermally formed intermetallic phases.

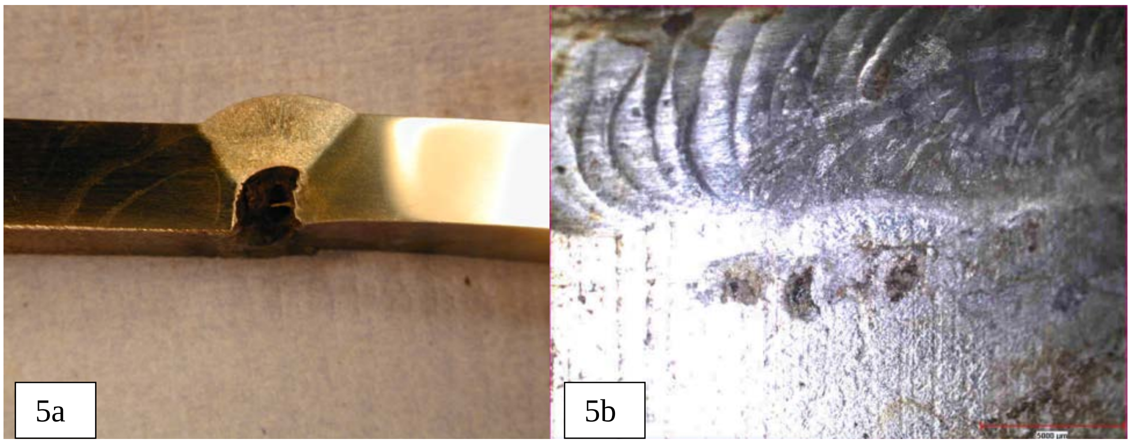


Figure 5: a) Weld Root Run Corrosion and b) LTHAZ Corrosion Attack

Apart from intermetallic phase formation the corrosion resistance of the root runs of welds can be compromised by over purging the bore of the pipes with Argon during welding[23] in a desire to minimize heat tint of the root. In such cases the nitrogen gas in solution in the molten weld metal can diffuse down the concentration gradient between the liquid metal and the Argon backing gas it's in contact with. This depletes the root run Nitrogen content and hence it’s PREN. This reduces the pitting corrosion resistance of the deposit. It possible to take shallow drilling from the weld root and measure the loss of nitrogen, this can be as much as 0.08% (a reduction in PREN of 1.28). This leads to preferential attack of austenite in the weld root (Figure 7).

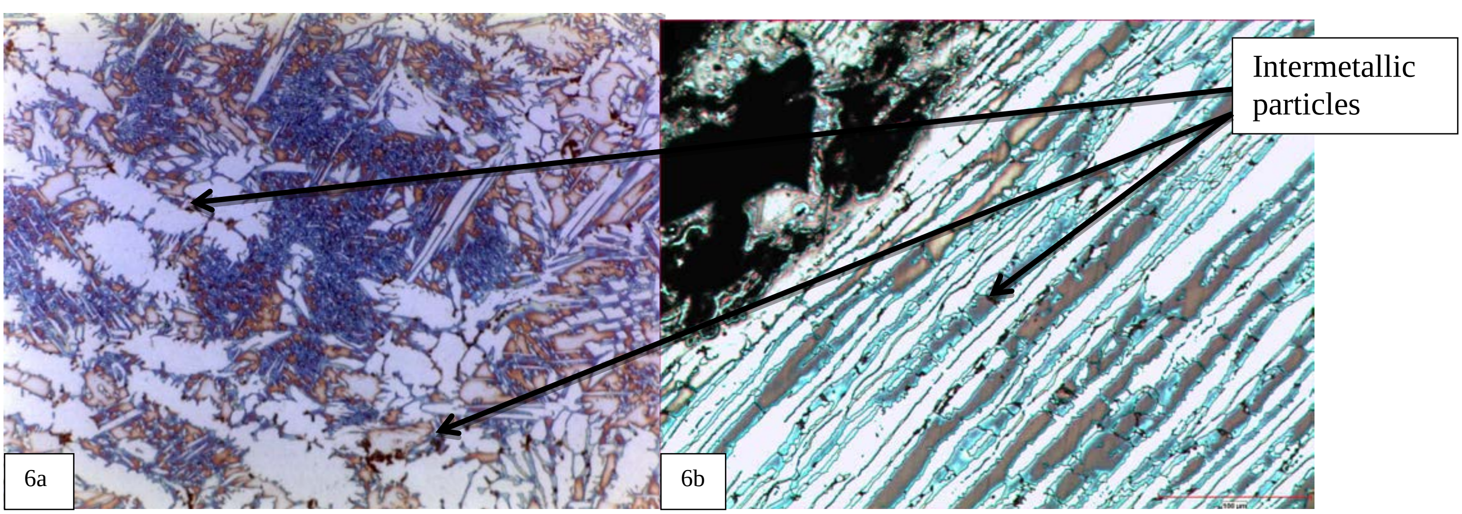


Figure 6: a) Weld Metal and b) LTHAZ Intermetallic Particles (samples etched electrolytically in Oxalic Acid and Potassium Hydroxide)

This is because Nitrogen partitions to the austenite phase, so Nitrogen loss reduces the corrosion resistance of this phase. This is a very commonly encountered problem when fabricators have difficulty qualifying a weld procedure. Remedial steps include controlled air leaks in to the backing gas (as air is 80% Nitrogen[24]) to lower the Nitrogen concentration gradient between the backing gas and the molten root pass, More commonly Argon/Nitrogen as a shielding gas mixes are used[25]. This alloys the weld metal with nitrogen through the torch. However, it also increases the Nitrogen concentration gradient between the root run and backing gas, so the rate of diffusion of Nitrogen out of the root can be higher.

Figure 7: Preferential Attack of Austenite in the Weld Root (samples etched electrolytically in Oxalic Acid and Potassium Hydroxide)

While the use of Argon/ Nitrogen shielding gas mixes is usually beneficial, it is because of the associated increased diffusion rates that its effectiveness in improving corrosion resistance is not always as high as anticipated. It has been found that the use of Argon/Nitrogen shielding gas in conjunction with Formiergas[†] ("F Gas", 90%N_2 +10%H_2) as a backing gas increases the retention of Nitrogen in the weld deposit and hence the PREN and the corrosion resistance of the deposit (Figure 8). CPT's in ferric chloride solution of 50ºC for manual GTAW pipe butt joints can be realised[26]. The weld metal microstructure of the root run and weld cap of welds deposited with Argon +2.5% Nitrogen

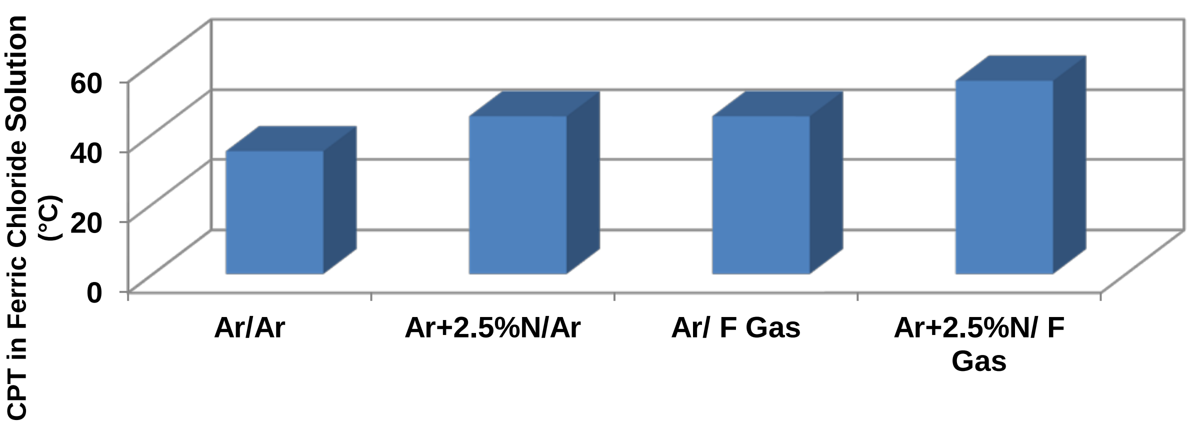


Figure 8: the Effect of Shielding Gas/ Backing Gas Combinations on CPT of Welds in Ferric Chloride Solution

Shielding gas and F gas as the backing gas are much more austenitic than the corresponding welds made under the same conditions using Argon for both shielding and backing gas (Figure 9). From comparison with similar work[27] it appears that the increased nitrogen content makes the weld metal less sensitive to intermetallic formation and more tolerant of higher heat inputs (Figure 10).The use of F gas also provides a very low level of heat tint of the root of the weld and this may contribute to improved corrosion resistance also. Although pick up of Hydrogen by the weld metal is minimal (4ppm to 4.4ppm[26]) and ferrite contents were reduced, but the possibility of hydrogen embrittlement of restrained joints in process pipe work or with Cathodic Protection is a concern. However, for topside seawater systems the use of these gas mixes appears to be an attractive way of increasing the corrosion resistance of welded joints and avoiding leaks.

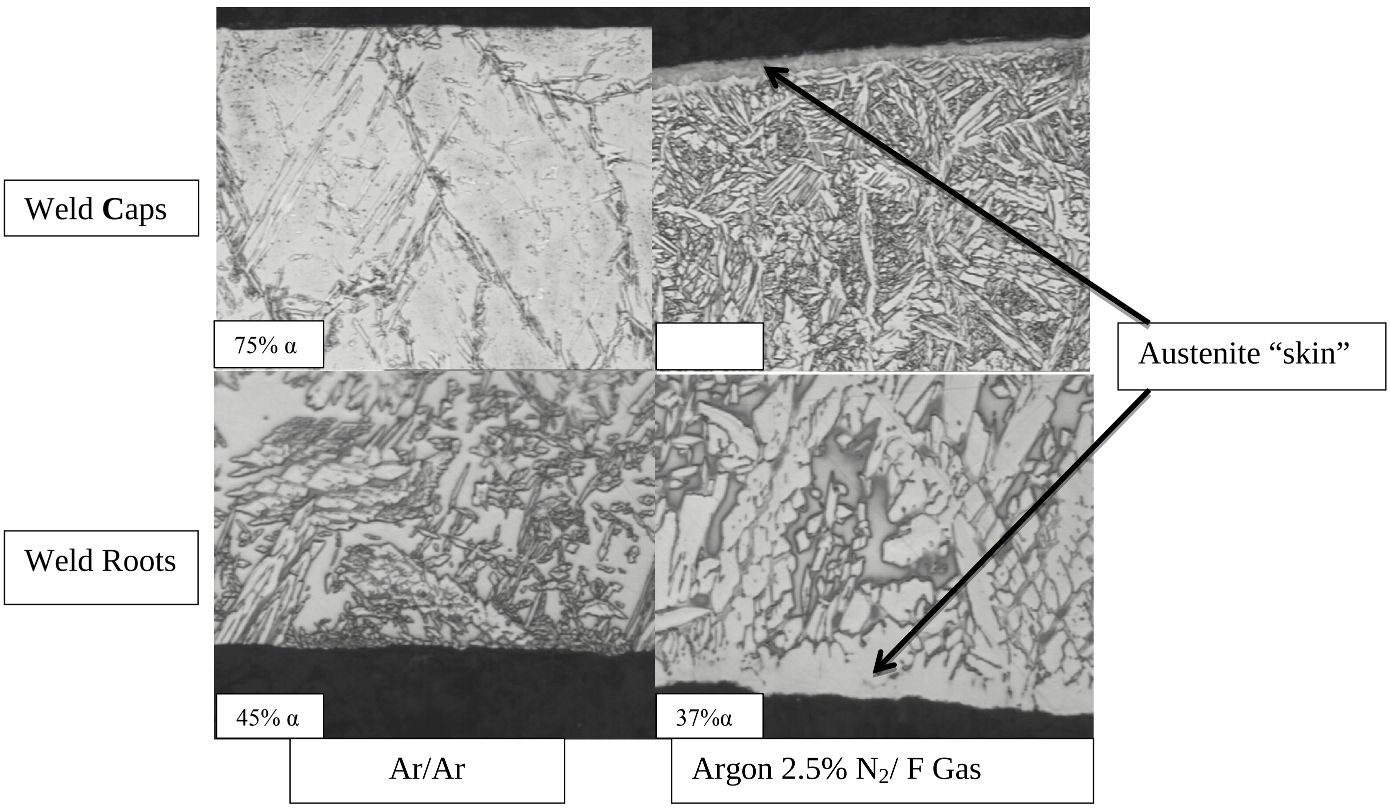


Figure 9: The Microstructures of Welds Deposited Using Pure Argon for Both Shielding (Ar/Ar) and Backing Gas and Argon +2.5% N_2 Shielding and F Gas backing gasses (samples etched electrolytically in Oxalic Acid and Potassium Hydroxide)

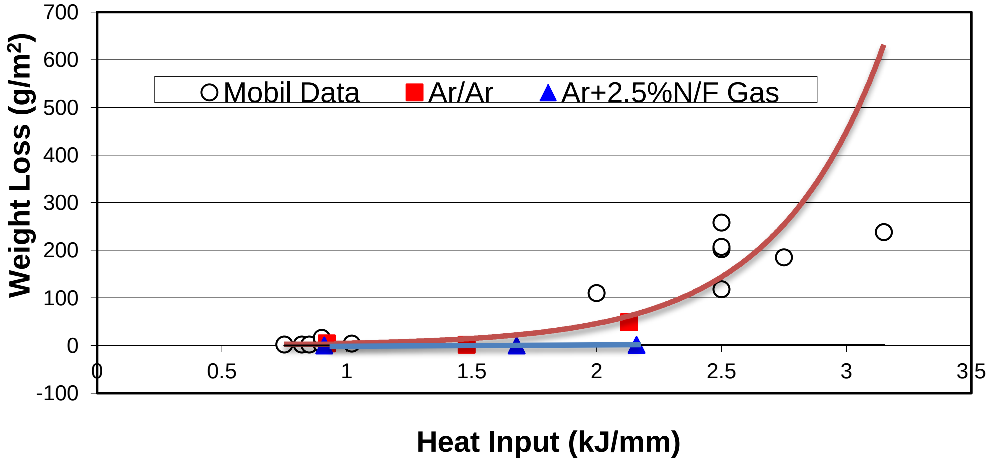


Figure 10: The Variation of Weight Loss Results of Welded Joints made with a Range of Heat Inputs and Welding Gas Combinations when Exposed to Ferric Chloride Solution at 40°C for 24 Hours

The corrosion resistance of welds can also be enhanced by acid pickling of the joint[28]. Figure 11 shows that the CPT of well made, "as deposited" welds has a minimum of 45ºC at about +600mV SCE. Hence, the suggestion that the temperature limit for these steels in chlorinated seawater with a residual chlorine content of 0.8ppm maximum should be 40ºC.

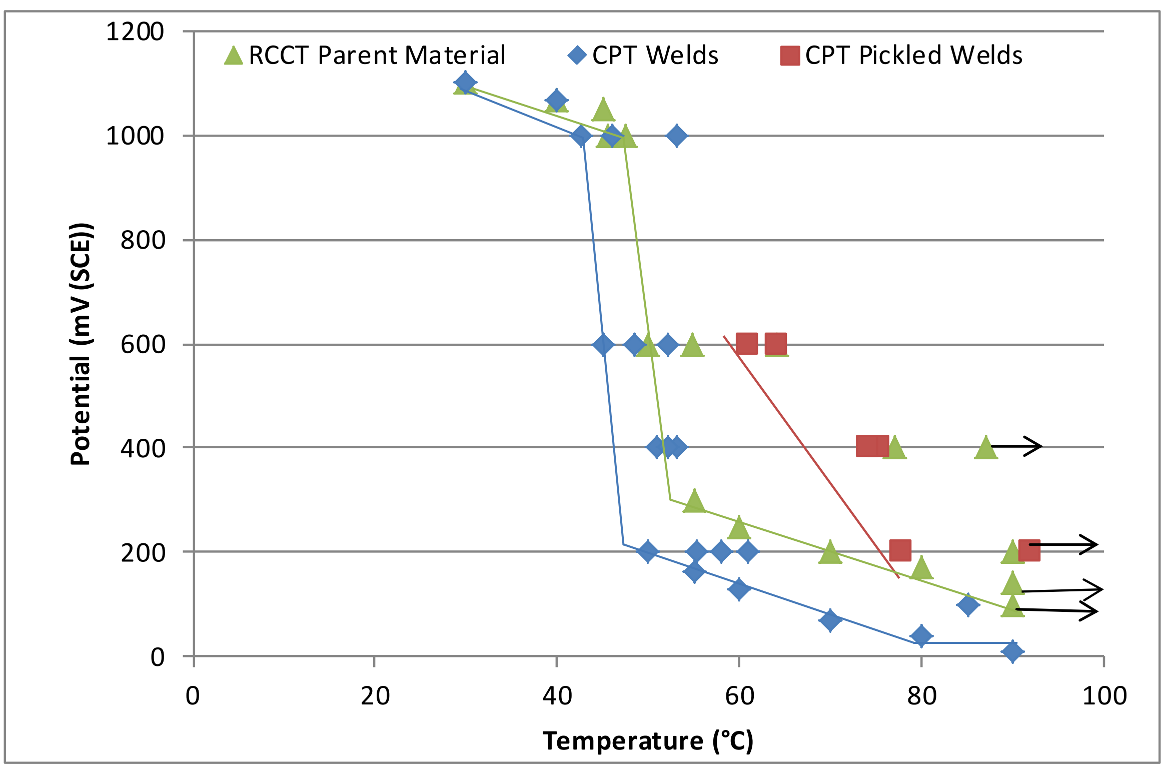


Figure 11: Variation of RCCT of Parent Material and CPT of "As Deposited" and Acid Pickled Welds in Seawater Solution

However, with acid pickling of the welds the corrosion resistance of the joints can become higher than the crevice corrosion resistance of the parent material. This means that for chlorinated sea water systems the design temperature could be extended to say 45ºC. If as discussed above, low level chlorine dosing of 0.1 ppm maximum can be achieved then temperatures of the order of 65ºC can be achieved without corrosion as we have found[5]. It is interesting to note that acid pickling makes the passive film more robust and that this may be similar to the effect of “soft startup”. This work also emphasizes the importance of effective acid pickle of all parts during manufacture to ensure that any material denuded in Chromium during heat treatment is effectively removed and corrosion resistance is optimized.

Subsea Process Pipework Applications

The failure of a forged pipe connector (hub) deployed subsea, was the first reported incident of HISC of duplex stainless as a consequence of CP[29]. Figure 12 shows the microstructure of the steel in the around the crack. It consists of large, parallel grains of ferrite and austenite. The cracking runs through the ferrite phase preferentially. The ferrite phase also contains intragranular nitride precipitates. The original failure investigation did not consider the influence of chromium nitride precipitate on the failure mechanism, principally because the material met the project specification requirements in all respects. However, later work[30,31] demonstrated that nitride precipitates in sufficient quantity can reduce impact toughness (especially at lower test temperatures), increase ductile brittle transition temperature, and reduce pitting corrosion, sulphide stress corrosion and HISC resistance of these steels. The HISC susceptibility of these steels is now managed by design codes that through a combination of reduced pressure ratings and designing components based on maximum strain level of 0.5% keep the material below the threshold level at which cracking is initiated.

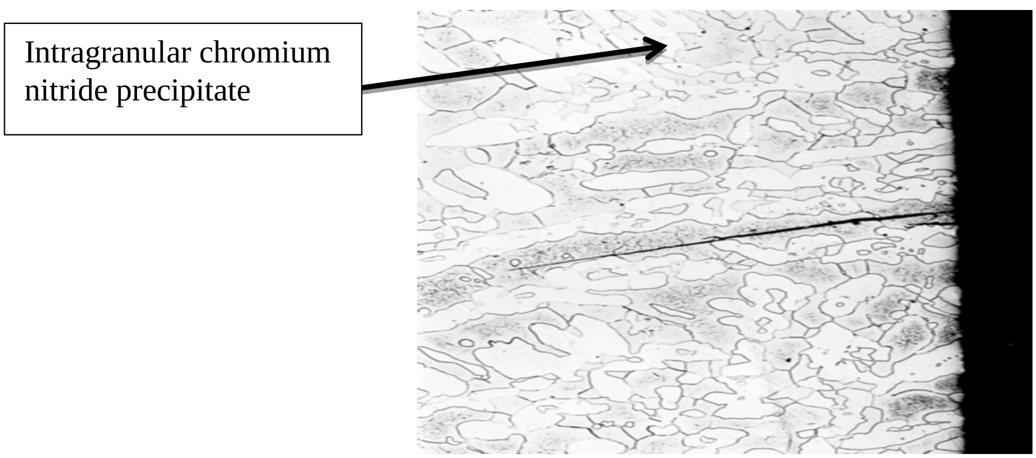


Figure 12: the Microstructure in the Region of Cracking of Failed Hub connector (etched electrolytically in Oxalic Acid and Potassium Hydroxide)

However, it is now possible also improve the inherent HISC resistance of the material through close control of alloy chemistry, forging processes and modified heat treatment practice to attain HISC threshold stress levels of 97.5% of the actual 0.2% proof strength of the material (Figure 13)[32]. By comparison, the original Foinavon material had a HISC threshold of 85% of actual proof strength, and conventionally manufactured Z100 product has a threshold of 95%. The Z100 modified product has a minimal amount of intragranular chromium nitride precipitate. This is because the alloy is metallurgically engineered and processed to take nitrides back in to solution and precipitate intragranular austenite instead of chromium nitride (Figure14).

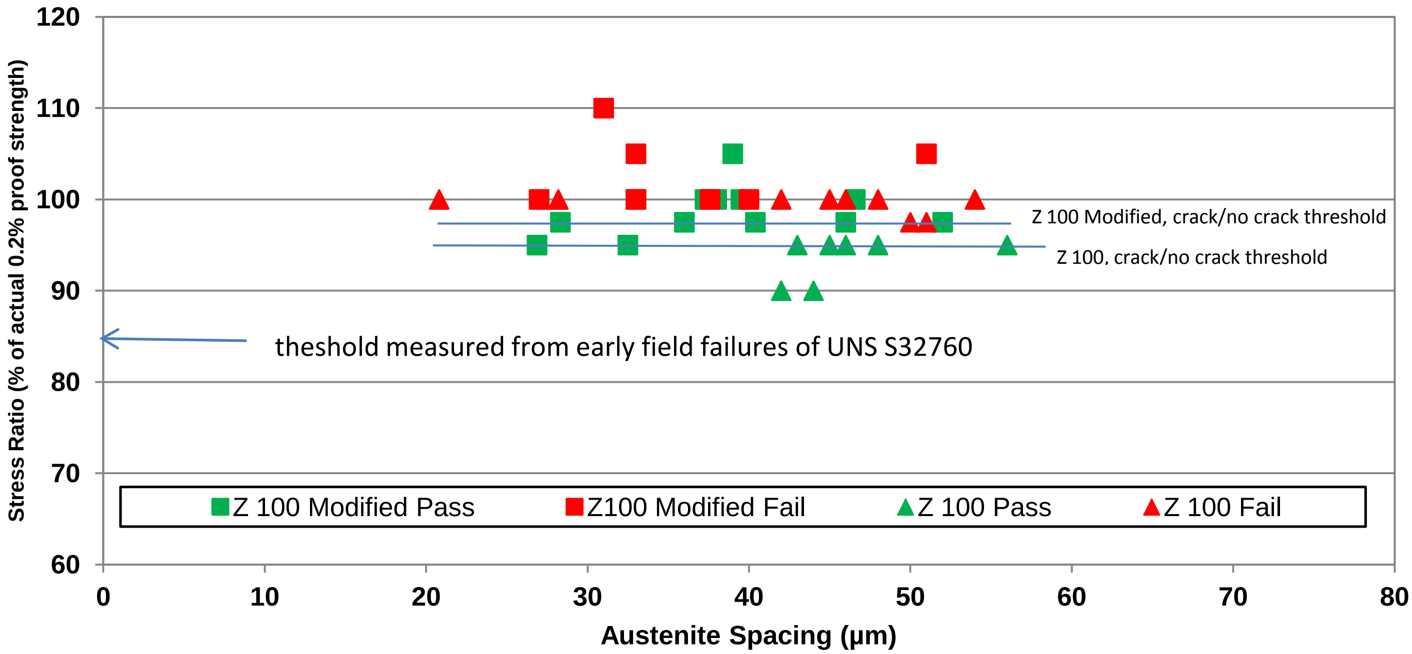


Figure 13: Summary of Constant Load Tests of Z100 and Z100 modified Samples from Forged 10k Weld Neck Flanges Exposed to Seawater and Polarized to -1.04V (SCE)

This improves both HISC resistance and impact toughness. Table 1 shows the location of samples and Charpy impact energy levels measured at test temperatures of minus 70°C. Weld Procedure Qualification Testing has also been carried out. This has shown that the HAZ toughness is retained to a level that is also suitable for minus 70ºC applications. The significance of this is that not only is HISC resistance improved but it also allows these grades to be used subsea in choked applications where Joule- Thompson cooling can generate very low metal temperatures under blow down conditions[33]. This avoids the cost impact and other problems associated with the use of alloy 625 (UNS NO 6625) in these applications.

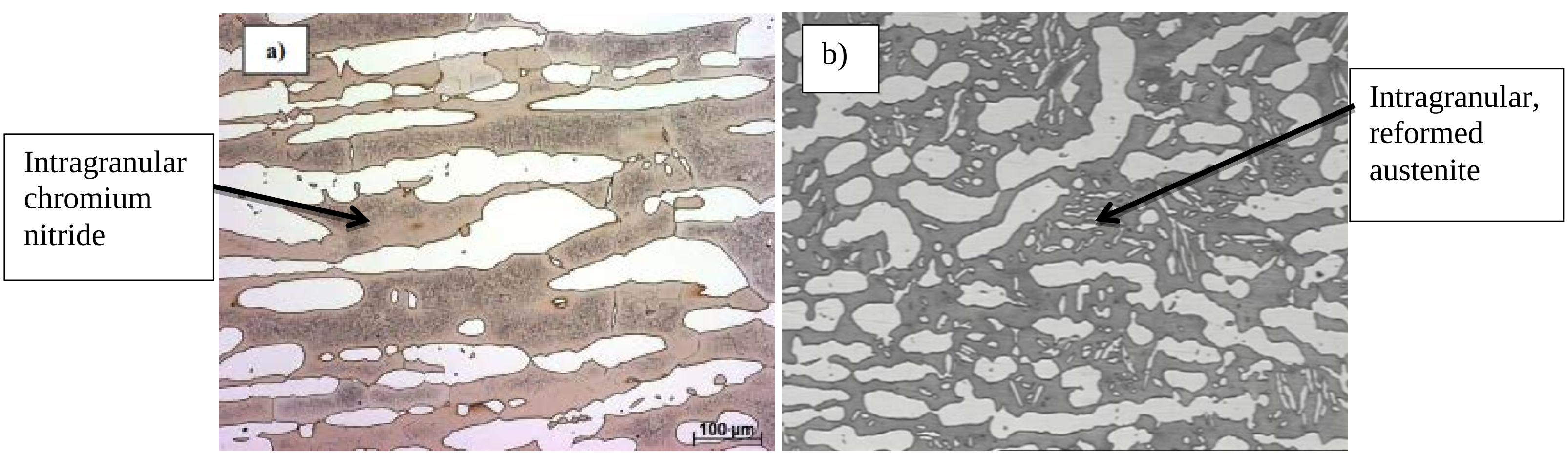
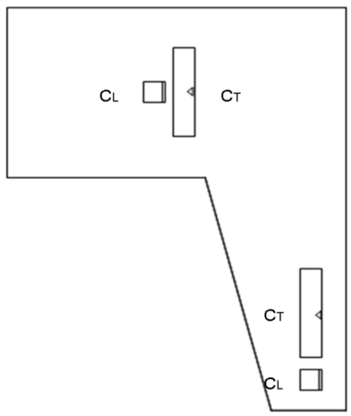


Figure 14: The Microstructure of a) UNS S 32760 Forging with a High Level of Intragranular Chromium Nitride Precipitate[31] and b) a Z100 Modified Forging with Intragranular Reformed Austenite (etched electrolytically in Oxalic Acid and Potassium Hydroxide)

Table 1 the Location of Test Samples and Distribution of Charpy Impact Energy Test Results at minus 70ºC from a 130.175mm 10k weld Neck Flange Forging



Position	1	2	3	Ave
Body C_L	223	276	235	245
Body C_T	84	167	180	144
Neck C_L	154	110	113	126
Neck C_T	283	297	297	292

Summary and Conclusions

Some of the less high profile, but never the less recurring, problems associated with Super Duplex Stainless Steels in offshore oil and gas applications have been discussed. Crevice corrosion of flange faces can be resolved by better selection and control of use of gasket materials, avoidance of galvanically incompatible parts, control of temperature, level of chlorination and start up procedure. Moreover, the use of Tungsten and Copper bearing grades can give some protection against corrosion due to transients in operational conditions because of the way that they readily repassivate compared to other grades.

It has been shown that the corrosion resistance of threaded connections can be enhanced by acid softening and pickling to remove surface layers that are more prone to corrosion attack.

Weld metal and LTHAZ corrosion attack have been considered. Optimum quality materials of construction and disciplined fabrication procedures and welders are required for the fabricator to be successful. But the use of different shielding and backing gas combinations to militate against Nitrogen loss to the backing gas does improve corrosion resistance and appears to extend the range of heat input that can be applied before damaging amounts of intermetallic particles are precipitated. Acid pickling of the process faces of welded joints can also be used to optimize corrosion performance of well-made joints.

Indeed, it is proposed that if applied diligently these processing changes and changes to start up procedures can significantly improve the resistance of the total pipework system to seawater corrosion attack not only making them more robust but they may well be utilized to expend safe operational limits.

We have also considered subsea process environmental challenges for these alloys. The precipitation of chromium nitrides in these steels limits their toughness, resistance to HISC and other important properties. We have shown that with the correct alloy chemistry and processing, detrimental nitrides can be transformed in to the beneficial austenite phase. This improves low temperature impact toughness and HISC resistance.

To conclude, we have shown cases where some of the weaknesses of these steels can, with proper processing, be converted in to benefits. It is hoped that these concepts can be taken on board and built in to corrosion management strategies such that new projects would be much less likely to experience repeat problems and may even be able to realize safe limits of use enhancements for critical applications.

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References

1. Shone B. et al. “ Stainless Steels as Replacement Materials for Copper Alloys in Seawater Handeling Systems” Trans. Inst. Marine Engineers, Vol.100, p193, 1998
2. Strandmyr O. and Hagerup, “Field Experience with Stainless Steel Materials in Seawater Systems” Proc Conf. NACE, Corrosion ’98., Paper 707, March 1998
3. Shrive S. “Seawater Materials – The British Experience” NITO’s 12th Symposium on Corrosion and Materials Offshore. Stavanger, Norway. January 1999
4. Strandmyr O. “Seawater Materials-The Norwegian Experience” NITO’s 12th Symposium on Corrosion and Materials Offshore. Stavanger, Norway. January 1999
5. Francis R. and Byrne G. “Stainless Steel World. Vol. 16, p53, June 2004
6. Francis R. and Byrne G. “ Experiences with Super Duplex Stainless Steel in Seawater” Proc. Conf. NACE, Corrosion 2003, San Diego, California, USA, Paper 03255, March 2003
7. Francis R. Irwin J. and Byrne G, “The Repassivation of High Alloy Steels in Chlorinated Seawater” Brit. Corr. Journal. Vol. 30 , No 3, p237
8. Valen S. Gartland PO. and Steinsmo W. “ Marine Corrosion of Stainless Steels: Chlorination and Microbial Effects” European Federation of Corrosion Publication No. 10, p114, Institute of Metals, London, 1993
9. Gartland P.O. and Drugli J. M. “Crevice Corrosion of High Alloyed Stainless Steels in Chlorinated Seawater” Proc. Conf. NACE. Corrosion ’91. Cincinnati, Ohio, USA. Paper No.510 March 1991
10. Gartland P.O, “ Marine Corrosion of Stainless Steels: Chlorination and Microbial Effects” European Federation of Corrosion Publication No. 10, p134 Institute of Metals, London, 1993
11. Natishan P. M, Martin F. et al. “Repassivation of Localized Corrosion Damage Using Cold Chlorinated Salt Water” Proc. Conf. NACE. Corrosion 2007, Nashville, Tennessee, USA. Paper 6281, March 2007.
12. Egan F. “Service Experience Of Super Duplex Stainless Steel in Seawater” Stainless Steel World, Vol 9, No10, p61-65, December, 1997.
13. Walleen B. and Andersson T. “Galvanic Corrosion of Copper Alloys in Contact with Highly Alloyed Stainless Steels in Seawater” Proc. 10th Scandinavian Corrosion Congress. Stockholm, Sweden. Paper No. 29, p149
14. Francis R. and Byrne G. “Factors Affecting Gasket Selection for Stainless Steels in Seawater” Proc. Conf. NACE, Corrosion 2007, Nashville, Tennessee, USA. Paper 07262, March 2007
15. Wallen B. and Henrikson S. “The Effects of Chlorination of Stainless Steels in Seawater” Proc. Conf. NACE, Corrosion’88, St Lewis Missouri, USA. Paper 403, March 1998
16. Rogne T. et al. “Crevice Corrosion Properties of Weld Overlays of Ni- Based Alloys Compared with 6%Mo Stainless Steels for Seawater Applications” Proc. Conf. NACE, Corrosion ’98, San Diego, California, USA. Paper 696, March 1998.
17. Gunn RN. “Intermetallic Formation in Super Duplex Stainless Steel heat Affected Zones” Proc. Conf. Duplex Stainless Steels ’97. Maastricht, The Netherlands, Paper 029, October 1997
18. Nustad G E. et al. “Resistor Controlled Cathodic Protection for Stainless Steels in Chlorinated Seawater” Proc. Conf. NACE, Corrosion2003, San Diego, California, USA, Paper 03082, March 2003
19. Rolled Alloys Welding Guidelines for ZERON 100, 2009.
20. Francis R. “Discussion on the Influence of Sigma Phase on General and Pitting Corrosion Resistance of SAF 2205 Duplex Stainless Steel” British Corrosion Journal. Vol 27, No. 4 p319

21. Wiesner C.S. Garwood S J and Bowden P. “The structural Significance of HAZ Sigma Formation in Welded 25% Cr Pipework” Proc. Conf. ASME, Offshore Mechanics and Artic Engineering. Glasgow, Scotland, United Kingdom. June 1993
22. Weisner C. S.”Toughness Requirements for Duplex and Super Duplex Stainless Steels” Proc. Conf. Duplex Stainless Steels ‘97 Maastricht, The Netherlands, Paper 107 October 1997
23. Lundquist B.et al. “The Influence of Different Welding Conditions on Mechanical properties and Corrosion Resistance of SAF 2205” Proc. Conf. Duplex ’86. The Hauge, the Netherlands. Paper 10, October 1986
24. Warburton G.R. Spence M. A. and Whittaker S. “The Effect of Welding Gas Composition on the Serviceability of ZERON 100 Super Duplex Stainless Steel” Proc. Conf. Duplex ’94. Glasgow, Scotland, United Kingdom. Paper 25, November 1994.
25. Blom J. K. ”Improving Properties of Welded Joints in Duplex Stainless Steels by Welding with Shielding Gas Containing Nitrogen” Proc. Conf. Stainless Steels ’87. Institute of Metals. York, United Kingdom. p123 to 125 October 1987.
26. Byrne G et al,” Optimisation of the Corrosion Resistance of Pipe Butt Welds in Super Duplex Stainless Steels” Proc. Conf. European Federation of Corrosion, Pisa, Italy, Paper 7805. Sept 2014
27. Mobil Beryl Project, Fire Water Refurbishment Project, Amon C., Private Communication, June 1898
28. Francis R. and Warburton G.W.” The Effects of Post Weld Surface Treatments on the Corrosion Resistance of Super Duplex Stainless Steel Welds in Seawater” Proc. Conf. NACE. Corrosion 2000.Orlando, Florida, USA. Paper 630. March 2000
29 Taylor T S. et al. “Foinaven Super Duplex Materials Cracking Investigation”, Offshore Technology Conference, Houston, Texas, USA. May 1999, Paper OTC 10965
30 Byrne G. et al. “Variation in Mechanical properties and Corrosion Resistance of Different Alloys within the Generic Designation UNS S 32760” Proc. Conf. Duplex 2000. Stainless Steel World, Houston, Texas USA. Paper 2052. February 2000.
31 Aursand M. Rorvik G. Marken L.A. and Kulbotten I.M. “ Experiences with Hydrogen Induced Stress Corrosion Cracking of Duplex Stainless Steel Components in Subsea Service with Cathodic Protection” Proc. Conf. NACE, Corrosion 2013, Orlando, Florida , USA , March 17th - 21st, 2013
32 Byrne G. et al. “ ZERON 100AFP Super Duplex Stainless Steel for Increased Low Temperature Impact Toughness and Resistance to Hydrogen Induced Stress Corrosion Cracking of API Forgings for Subsea Applications” Proc. Conf. Offshore Technology Conference Brazil , Rio de Janerio, Brazil. Paper 571, October 2013.
33 Busschaerts F. et al.”New Challenges for the Use of Duplex Stainless Steels at Low Temperatures” Proc. Conf. Duplex World , Beaune, France, Paper 2B II. October, 2010