Hydrogen Induced Stress Cracking (HISC) Resistance and Improvement Methods for Super Duplex Stainless Steels

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ABSTRACT

The paper reviews the history of HISC failures of duplex and superduplex stainless steels when deployed subsea and subject to cathodic protection (CP) at potentials around -1V SCE. The test methods applied to investigate the problem and subsequently used to develop current design codes that deal with HISC are reviewed. Data from these investigations is compared with other testing using the same cast and batch of bar product, but where controlled shot peening is used to induce compressive residual stresses in the surface of the test samples. Parent pipe material and cross welded samples of seamless pipes were also tested. Peened material showed a 10 to 15% improvement in the threshold stress to initiate HISC. The paper also discussed the Advanced Forging Process (AFP) production route, recently developed to provide both increased notch toughness at low design temperatures and improved resistance to HISC in forgings used to make 10k weld neck and swivel ring flanges for subsea manifolds. Data is presented showing an increase in the threshold stress ratio (applied stress divided by the actual 0.2% proof strength) from 85% to 97.5%. We also find a corresponding increase in impact toughness of AFP material, allowing use of the products at design temperatures down to minus 70°C. This is attributed to the dissolution of detrimental nitride precipitates within ferrite grains in the forgings and transforming these into advantageous intergranular reformed austenite.

Key Words; *superduplex, HISC, toughness, forgings, residual stress, shot peening,*

BACKGROUND

Duplex and superduplex stainless steels have been deployed subsea with cathodic protection since the mid 1970's[1]. However, in 1996 the Foinaven(†) project[2] was the first reported case of stress corrosion cracking of a duplex stainless steel (in this case superduplex), while subsea and exposed to CP at levels of around - 1V SCE. Previous work using slow strain rate testing[3,4] had shown that these grades were susceptible to hydrogen embrittlement when exposed to CP potentials below -700mV SCE. However, it appeared that cracking only initiated at stresses of yield point or above and requires stresses approaching the Ultimate Tensile Strength (UTS) to propagate. The cracks ran through the ferrite grains and they were blunted and to some degree arrested by any austenite grains that they encountered. Based on this and the previous history of successful deployment, most projects did not consider hydrogen embrittlement due to CP to be a practical concern. So, the Foinaven problem, at the time, did come as a surprise. However, one pipe line project[5] had already deployed a Shottky diode system to retain pipeline cathodic protection potentials at a level where the duplex stainless steel was in the passive range and that was also well below the hydrogen evolution potential. Such systems were then not easily applied to manifold arrangements where the CP system is designed to protect carbon steel structures also.
The Foinaven problem was recognised during subsea hydrotesting, prior to start up, after 6 months underwater, when pressure could not be maintained. Previous, land based, hydrotesting was satisfactory, so there was a clear "delayed" nature to the cracking behaviour, which is commonly associated with the involvement of hydrogen gas in the failure mechanism. It was found that two hub connector forgings, located at one corner of the manifold (Figure 1), and had suffered cracking.

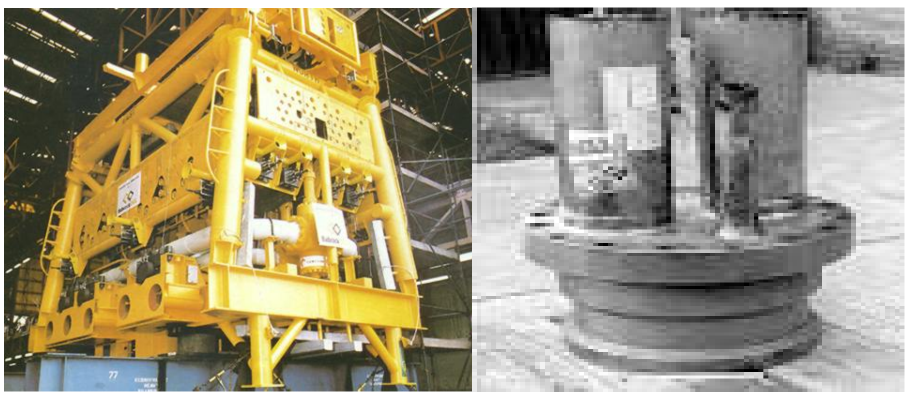


FIGURE 1: Manifold assembly and detail of the hub connector and attached pipework

These connectors were machined from a roughly 250kg piece weight top hat forging in grade UNS S32760. There was a total of 198 such forgings deployed subsea. The cracking was found to be located in a butt weld nipple that had been machined from the upset end of the forging to allow pipes to be easily joined to the connector by welding. The cracking was adjacent to, but not associated with the welded joint (Figure 2). The orientation was such that large ferrite grains ran across the wall thickness of the nipple. These provided long crack paths, uninhibited by austenite which would block the propagation of cracks[3, 7]. The brittle nature of the cracking, the retention of a good level of toughness and ductility in the bulk of the forging, the delayed nature of the cracking, the absence of corrosion attack and the presence of hydrogen gas due to cathodic protection caused the investigators to conclude that the failure mode was hydrogen induced stress cracking as opposed to hydrogen embrittlement. The microstructure of the steel also exhibited nitride precipitates within the ferrite grains. At the time these were not considered a contributory factor, as the suite of Charpy Impact testing and ferric chloride corrosion testing applied to the forging (and then reapplied to the cracked hub forging) all

† Trade Name.

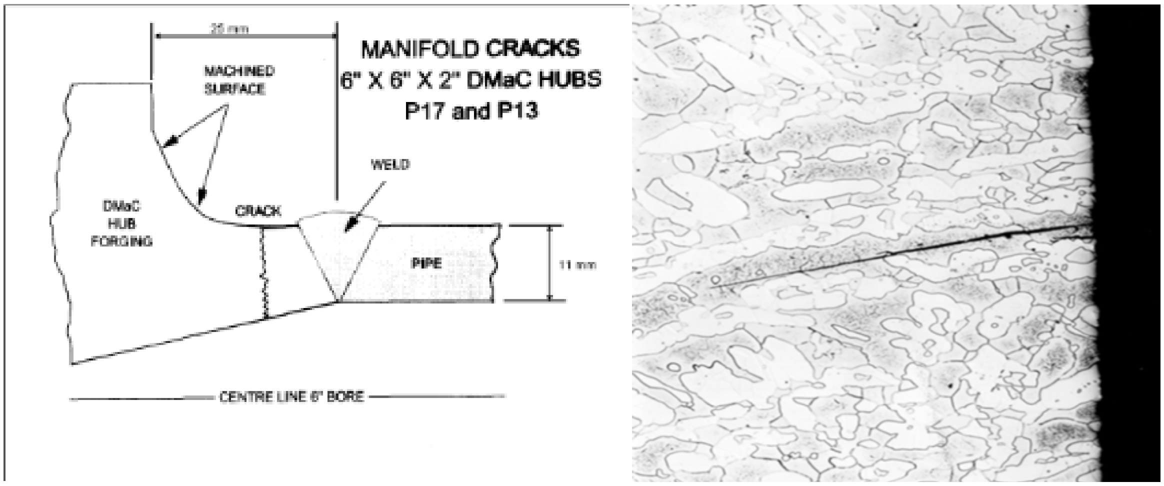


FIGURE 2: Showing the location and detail of cracking found in the hub forgings.

readily met the project specification requirements. However, later work[8] did find high levels of nitride reduced the HISC resistance of duplex stainless steels. It took months of work to reproduce the Foinaven failure in the lab[9], to confirm the failure mechanism, and complete the mechanical engineering exercise required to determine if the equipment in place was fit for service or needed to be replaced or modified.

Other factors also contributed to the Foinaven failure. The coating systems were found to be very poor, blistering before the project had become operational, exposing more surface of the duplex steel to full CP. It also transpired that the manifold had been dropped in a skewed orientation during installation, with one corner of the manifold landing on the seabed first causing a stinger to shear off from the structure. It was the hub connectors located at this corner that cracked and had to be replaced. Mechanical engineering evaluations were combined with HISC testing results to establish safe operational conditions for the project and this confirmed that the project could proceed without restriction to production. None of the other 196 hub forgings were cracked or had to be replaced. Remedial work was done to the coating systems to provide better insulation. The facility has operated without any recurrence of this problem since that time. Interestingly, the use of hot isostatic pressing (HIP) as a manufacturing route for the hubs, even though it was known to be highly resistant to HISC[6] because of its fine grain size, was dismissed by the EPC contractor because of then perceived weldability issues with the HIP product.

Shortly after Foinaven, the Britannia[(†)] Project 22%Cr duplex stainless steel manifold also suffered HISC. In this case the material of construction was also found to be good in all respects. There was no complication of unusual grain size, grain orientation or presence of nitride precipitates, but the manifold did have some pre-existing cracking in welds that was not detected prior to installation. This was evident because coating products were subsequently found on the fracture face. The manifold was mounted on a subsea plinth and the flow line that came of the manifold was laid in a trench and back filled to avoid movement along the sea bed (so called rock dumping). However, the position of the sea bed was misjudged and when the trench was backfilled this caused plastic deformation, disbondment of the coating system and extension of the pre-existing cracking at a bend in the pipe coming off the manifold[10].

Other subsea failures due to CP of super ferritic[13] and duplex stainless steels[14, 15] (one of which is very similar to Foinaven) followed and DNV [(†)]–RP- F112[11] was developed. This standard provides a design approach, for duplex stainless steels, its implications have been reviewed by Turbeville[12]. However, very little effort seems to have been made to develop methods of manufacture to improve HISC resistance and increase the utilisation thresholds defined by F112 or provide a higher margin of tolerance to HISC than is currently the case. This paper now presents some methods of improving HISC resistance of these steels.

TEST METHOD

Tensile test samples were taken from 150mm NB XXS seamless pipe, 130.17mm API[(†)] 10k forged weld neck flanges, 12.5mm, 114.3mm and 160mm diameter bars in superduplex stainless steel grade UNS S32760. Similar samples were taken from across the weld of a superduplex stainless steel welded joint made in 150mm NB Sch 120 seamless pipe. These were tested in the as-machined and shot peened condition. The peening applied was with hardened steel shot (0.584mm diameter and 55 to 62 Rockwell C) to military spec MI 230H. The shot velocity was 49 m/ s. During peening full coverage was ensured by using marking blue that disappears when peened. This was done twice (200% coverage) to ensure the surface was fully peened. An Almen intensity strip was also preened in parallel with the samples. During peening this strip deforms and bends upward. This deformation (arc height) is a measure of the residual compressive stresses induced in the surface by peening. This strip is dead mild steel, 1.29mm thick and gave a deflection of 300 microns mean. A computer model was also used to estimate the level of compressive residual stress induced in the samples and micro hardness measurements were made to determine the depth of penetration of the peeing below the surface of the sample. Using a test procedure developed by Woolin [9], samples were loaded in to a glass chamber and immersed in 750ml of synthetic seawater solution (pH adjusted to 7.8 to 8.2 with HCl or NaOH as detailed below.

0.2g/L Na HCO_3,
2.27g/L $CaCl_2.6H_2O$,
6.02g/L $MgCl_2.6H_2O$,
7.74g/L $MgSO_4.9H_2O$,
28g/L NaCl,
0.05g/L Na_2S,

The samples were then polarised to a potential of - 1.0 to – 1.1 V (SCE). They were stressed at a strain rate of 1x 10^{-3}/ sec up to various percentage levels of their actual 0.2% proof stress. These samples were then held at a constant load for 720 hours. After this they were cleaned and examined by liquid penetrant and subsequently by metallography for indications of cracking. The un-peened bar samples were tested independently by ourselves[8] and Wollin[9]. The peened bar samples were tested in our own laboratory. Separately, samples were also taken from 10k WN forgings made in the grade ZERON[(†)] 100 AFP. This is a product with controlled chemistry, forging and heat treatment practice applied[17]. These were subject to constant load testing to determine the HISC threshold stress ratio.

RESULTS AND DISCUSSION

The mechanical properties and austenite spacing's, as defined in reference 11, of the seamless pipe, 10k forgings and bars tested are shown in Table 1. All meet the requirements of the applicable specifications. The structure and properties of the bar products are reported elsewhere [8, 9]. However, to summarise, the 12.5mm diameter material can be considered "prime" while the 114.3mm and 160mm diameter bars contain increasing levels of nitride precipitate within the ferrite grains that impair their impact toughness, HISC resistance and other properties[8]. Table 2 shows the threshold stress ratio measured. The AFP material was not tested in the peened condition. It can be seen that the peening process has the effect of increasing the threshold stresses for cracking. It is known that peening introduces compressive residual stresses in to the surface of components [17]. Work on 4130 steel[18,19] also indicates that peening reduces hydrogen absorption and permeation rates. In this case, supplier modelling suggests that compressive stresses of around -700MPa were introduced to the sample to a depth of about 0.15mm decaying to zero about 0.35mm below the surface. Figure 3 shows a micro hardness profile measured across a section taken from two peened 12.5mm diameter bar samples. These profiles show that the effects of peening agree quite well with the computer model in terms of the depth to which peening extends in the samples. They also show that both the austenite and ferrite phases in the steel are similarly affected. Peening is commonly applied by the aerospace industry to improve the fatigue resistance of components like landing gear[17]. It is also reported to have some benefit with respect to stress corrosion cracking resistance[20]. In this study (Table 2) the 130.17mm 10k WN AFP material (controlled chemistry, forging practice and heat treatment regime) also shows improved resistance to HISC without being processed by peening when compared to regular forged product. This improvement in threshold has been confirmed by multiple tests as shown in Figure 4. A significant improvement in resistance is seen compared to the Foinaven material threshold. Current design rules cover material of this type but may be overly conservative for improved alloys like Z100 manufactured using AFP. However, HISC analysis methods are strain based so any benefit of improved thresholds would have to be considered on an individual component basis.

TABLE 1 Specimen Properties

FORM	0.2% PS (MPa)	Charpy Impact Energy @-46°C (J) (except where stated otherwise)			Ferrite (%)	Mean Austenite Spacing (µm)
150mm NB XXS pipe	636	100	105	126	52.4	19
130.17mm 10k WN (B1)	595	288	294	296	51.8	42
130.17mm 10k WN (B2)	575	65	76	82	54.3	46
130.17mm 10k WN (B3)	583	138	138	142	54.9	47
130.17mm 10k WN (Z100AFP) [CVN @-70°C]	565	233	276	235	50	46
12.5mm dia. bar	567	246	255	250	52	7.1
114.3mm dia. bar	578	155	168	158	43.9	25.7
160mm dia. bar	575	68	77	70	56.1	35.6

Table 2 Threshold Stresses for Pipe and 10k Forgings

Stress Ratio (% of actual 0.2 %PS)	150mm XXS Pipe			130.17mm 10k WN flange				
	Plain	Plain	Peened	Plain	Plain	Plain	Peened	Z100AFP
120			crack					
110		crack	no crack				crack	
100	crack	no crack		crack		crack	no crack	crack
97.5						crack		no crack
95	no crack			no crack	no crack	no crack		no crack
90	no crack			no crack	no crack			no crack

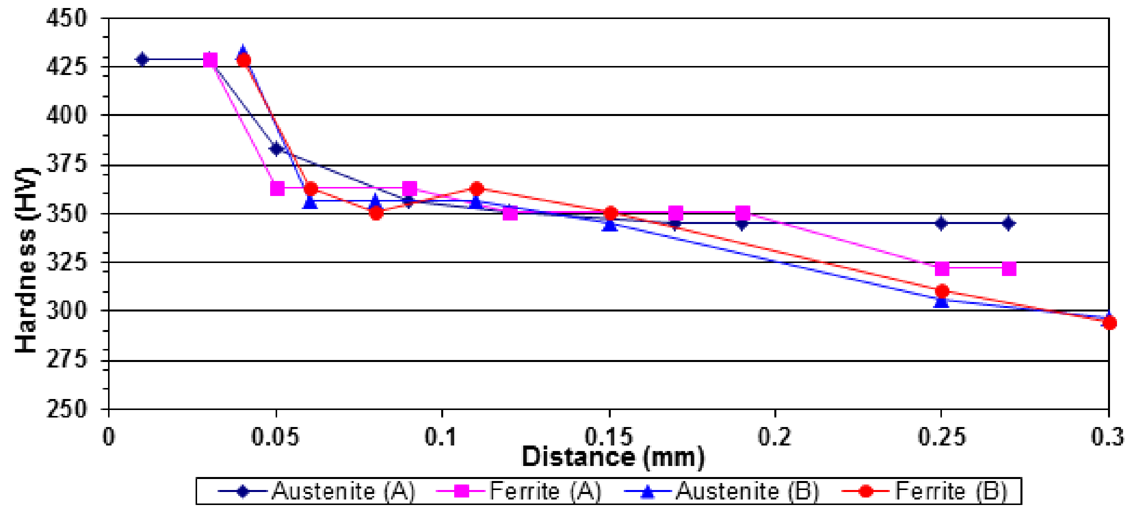


FIGURE 3: Micro hardness profiles (HV 25g) from surface of shot peened 0.5in diameter bar

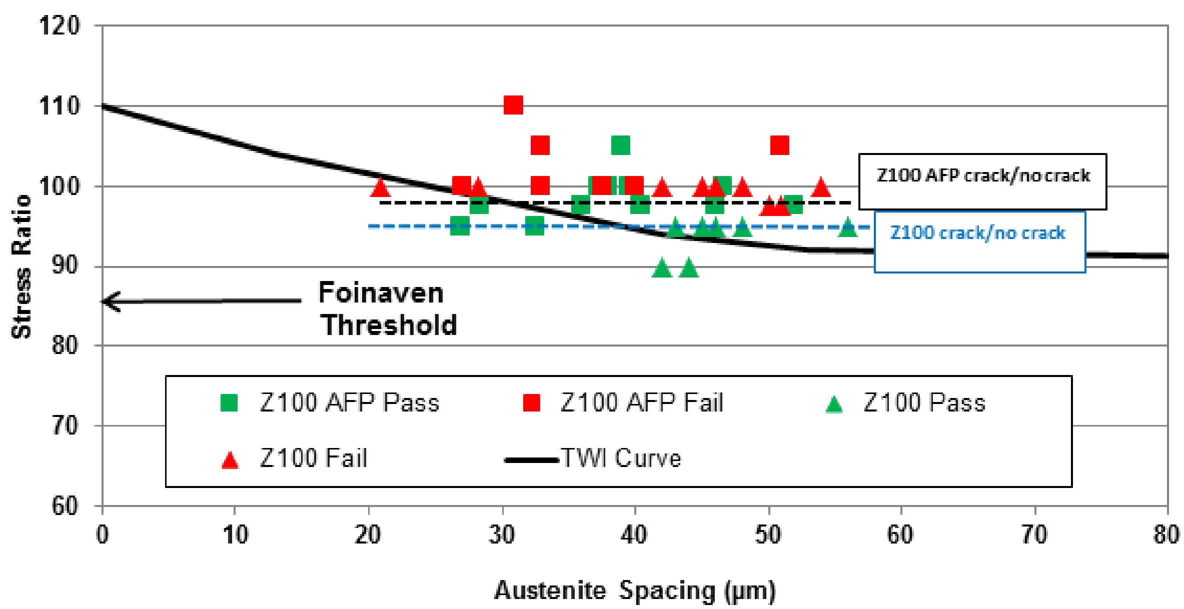


FIGURE 4: Summary of constant load tests of Z100 and Z100AFP forged products In seawater at -1.04V SCE

Figures 5 and 6 show the time to failure versus the stress ratio for the bar product samples both peened and un-peened. Figure 5 is typical of prime bar. Figure 6 is typical of material with nitride precipitates in the microstructure, these lower the threshold stress level for the onset of HISC. In both cases peening improves the resistance to HISC. Figure 7 shows the nature of the cracking observed in the un-welded samples. A non-propagating micro crack, typically one grain deep, constitutes the limit of detection in these tests. Figure 8 shows the time to failure versus stress ratio for a cross welded tensile specimen. Table 3 details the improvements in HISC threshold in percentage terms. It can be seen that the finer austenite spacing bar and pipe products appear to gain more benefit from peening than coarser spaced forged products. The observations made were, no cracking, short, apparently non-propagating cracks (about one grain deep) through to complete failure of the sample. It is reported that if cracking occurs it initiates early in the test when room temperature creep strains are highest[9]. This phenomenon of room temperature creep occurs under static, load control conditions. Were these tests displacement controlled then the creep would relieve the applied stress and the test would be less severe. The ability to control creep strains may prove to be significant in our ability to take further precautions to avoid HISC.

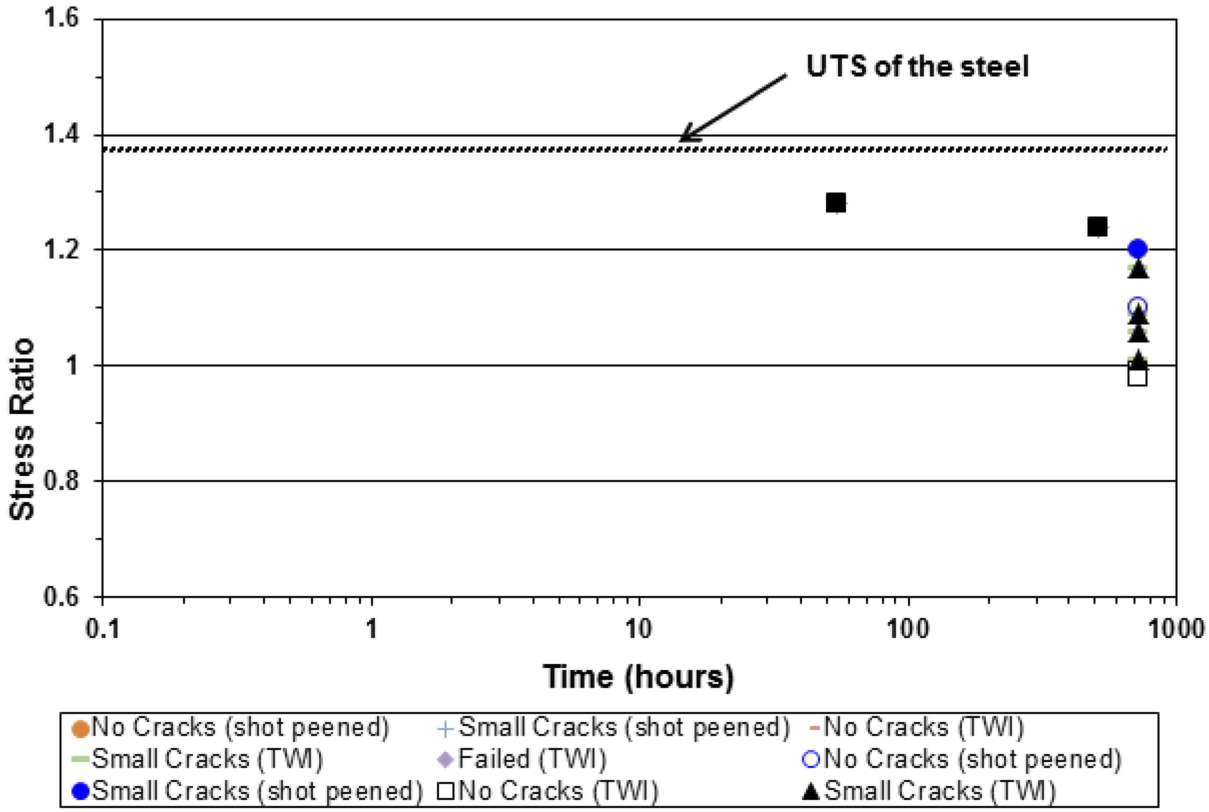


FIGURE 5: Stress Ratio versus time for 12.5mm diameter bar tested at -1.1V SCE in seawater

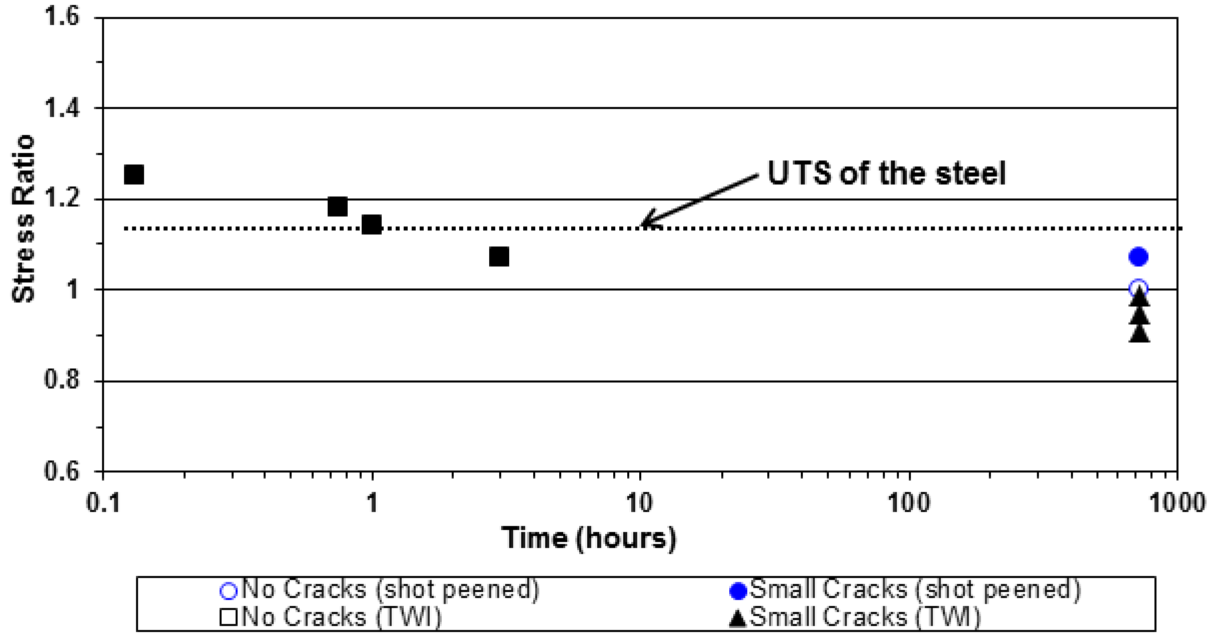


FIGURE 6: Relative stress versus time for 160mm diameter bar tested at -1.1V SCE in seawater

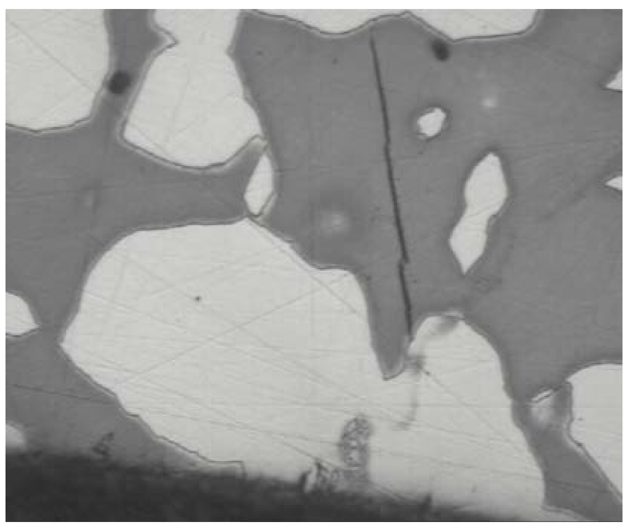


FIGURE 7: Micrograph showing crack one grain deep in parent metal (Etched electrolytically in oxalic acid and potassium hydroxide)

Figures 9a and 9b show typical HISC found in the welded samples. We also tested a sample with only half its gauge length peened to see if any areas missed by the process became more susceptible to cracking. Surprisingly this was not the case. No cracking was found at 102% of the proof stress and first crack initiation was first found at 106% of the proof stress. These cracks were found in the un-peened area away from the peened/un-peened interface. We would have expected the residual compressive stresses at the surface of the peened area to be balanced by corresponding tensile stresses in the adjacent un-peened area. However, these results appear to suggest that this stress balancing occurs through thickness rather than at the surface, across the peened/un-peened interface. We have assumed that the benefit of peening is attributable to compressive residual stresses. But it is also possible that peening may also affect the diffusivity of hydrogen gas into the material[18, 19].

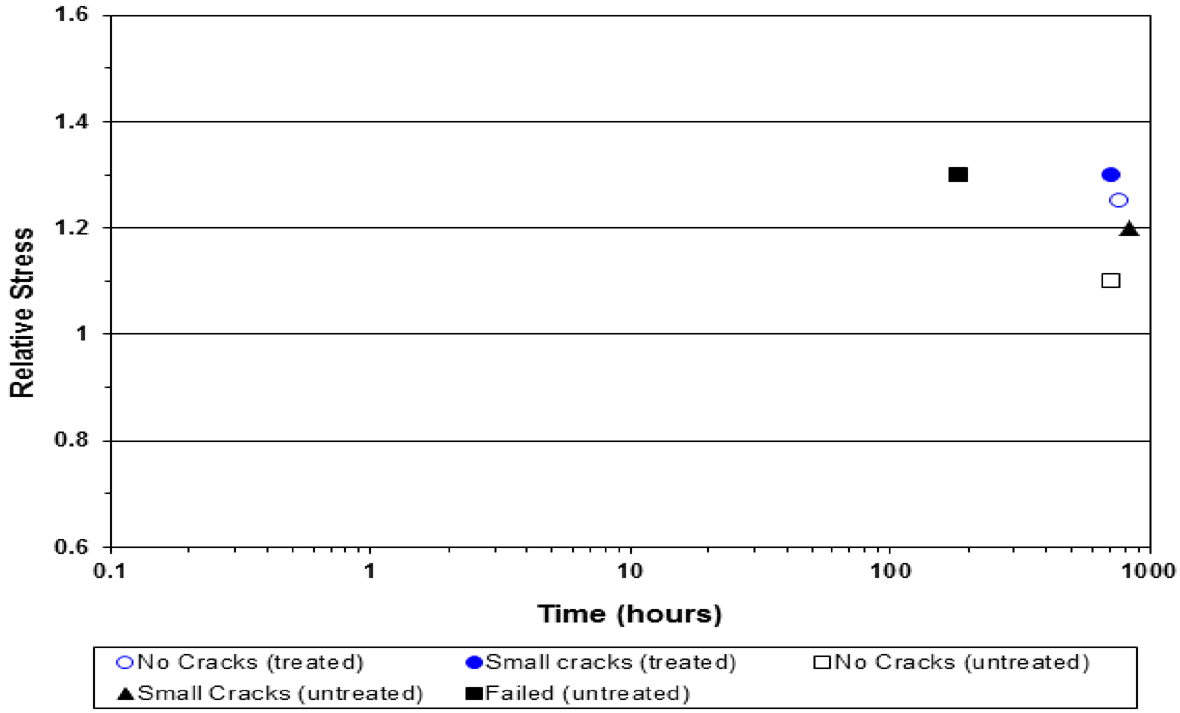
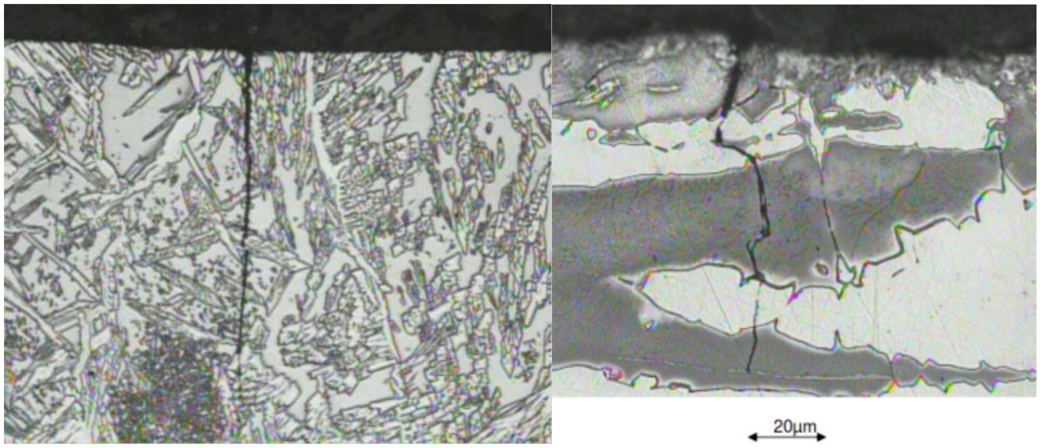


FIGURE 8: Relative stress versus time for welded Z100 tested at -1.1V SCE in seawater

Table 3 A Comparison of the threshold stress of peened and plain samples

Product Form	Threshold Stress (as a ratio of 0.2%PS)		% increase
	Plain	Peened	
12.5mm dia. bar	1	1.1	10
114.3mm dia. Bar	0.87	1	15
160m dia. bar	0.88	1	13
150mm NB XXS pipe	1	1.1	10
130.17mm 10k WN	0.95	1	5
X welded sample	1.1	1.25	14



a) Un-peened weld metal. b) Peened HAZ of weld

FIGURE 9: The appearance of cracking in the samples (Etched electrolytically in oxalic acid and potassium hydroxide)

Cracking in the un-peened cross welded sample was found in the weld metal (Figure 9a) whereas in the peened weld it was found in the HAZ (Figure 9b). A cross weld, peened sample was also subjected to 2% strain after peening in an attempt to simulate hydro testing. This strain cycle did not affect the HISC resistance of the peened sample.

Considering the AFP product, better control of alloy chemistry, steelmaking, and forging and heat treatment practice has been found to consistently provide improved impact toughness (Table 4).This enhancement makes the product suitable for application subsea where design temperatures may be as low as -70°C in cases where Joule Thompson cooling may apply. Typically, Charpy impact toughness levels specified for these products are 45J average at -46°C. Forgings exhibiting toughness levels in this range have been found to contain intragranular nitride precipitates (Figure 10). Forgings with this type of micro structure have been found to pass oil industry standard test requirements but have lower than expected levels of HISC resistance and also resistance to sulphide stress corrosion cracking. If levels of nitride precipitates are high, then toughness and pitting resistance in ferric chloride solution can fall below minimum requirements[8]. The propensity to nitride precipitation is a function of solution treatment temperature, coarseness of the austenite spacing and the nitrogen content of the grade. Higher nitrogen alloys, forged at higher forging temperatures, are more prone to precipitation of nitride particles and the precipitate is found to harden the ferrite grains (Figure 11)[21]. Higher hardness levels are commonly associated with lower toughness and increased susceptibility to stress corrosion cracking. The process controls for the AFP product, however, produce a rather different microstructure (Figure 12). In this case intragranular nitride is displaced by secondary austenite within the ferrite grains. This removes the precipitation hardening and local chromium depletion effects caused by the nitrides and replaces them with softer, tougher and more hydrogen absorbent austenite grains. The morphology of these grains may also have the practical beneficial effect of minimizing the austenite spacing too. However, no account of intragranular austenite is taken F112[11].

Recent work [22] has identified the role of forging temperature on dynamic recrystallization and recovery processes that appear to control dislocation networks that act as nucleation sites for nitride precipitates within the ferrite grains.

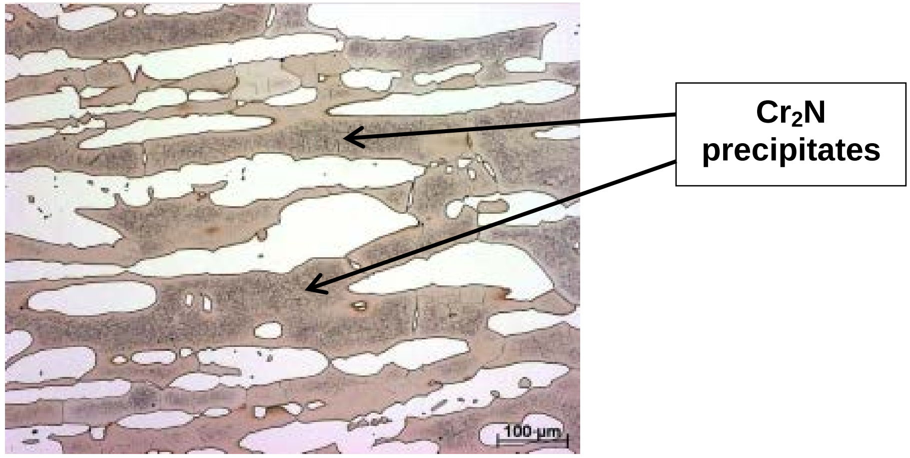


FIGURE 10: The microstructure of a flange forging showing nitride precipitation within the ferrite grains (etched electrolytically in oxalic acid and potassium hydroxide)

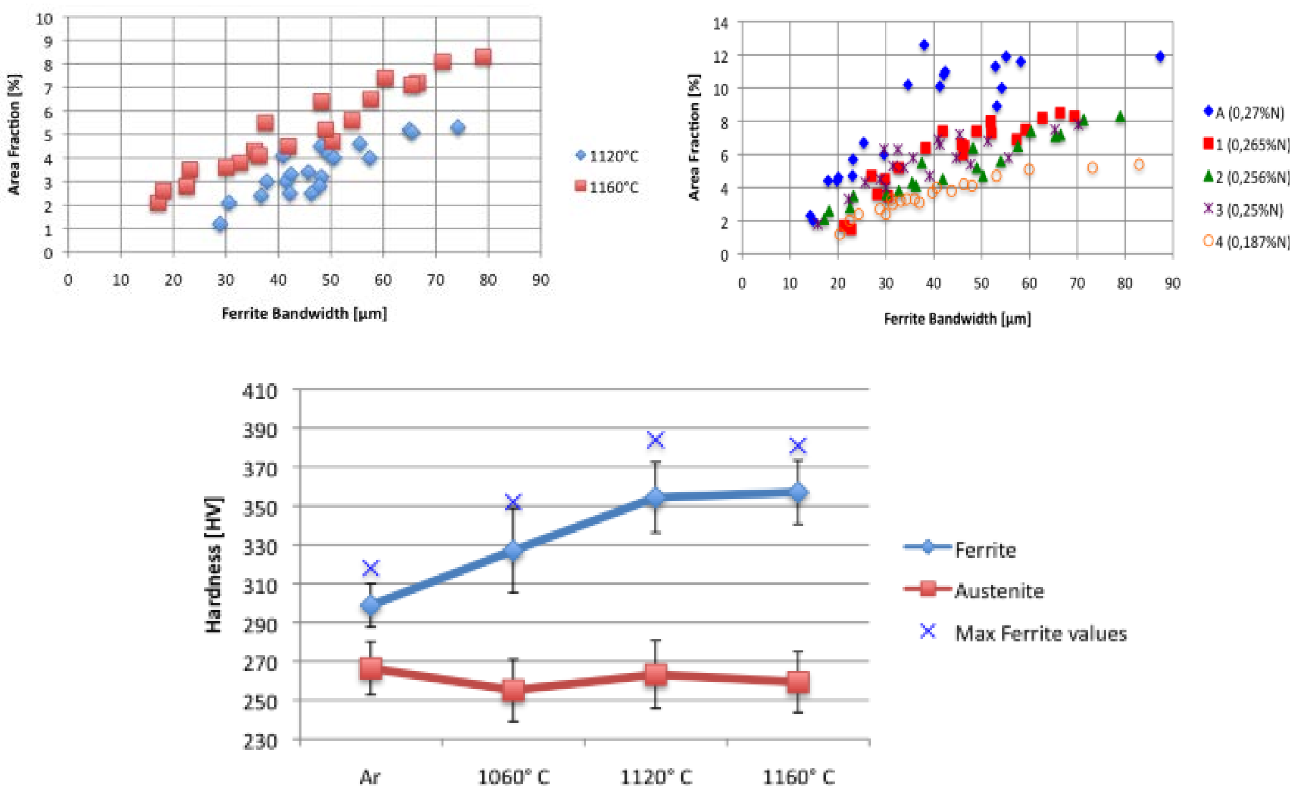


FIGURE 11: The effects of solution treatment temperature, austenite spacing and alloy nitrogen content on nitride area fraction of precipitate and micro hardness of the ferrite phase (After Iversen[21])

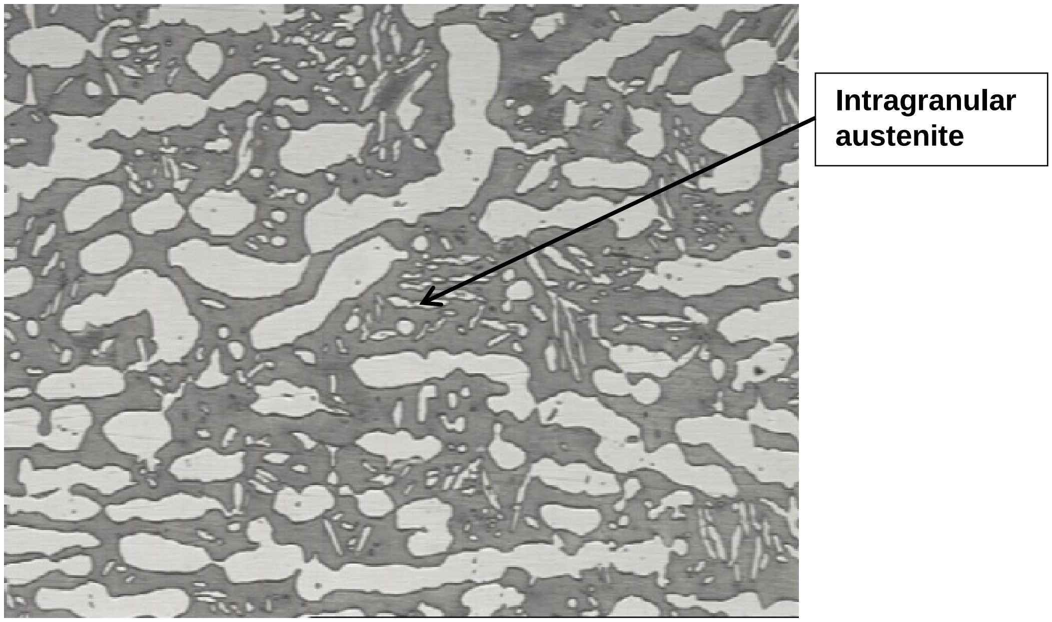


FIGURE 12: The microstructure of Z100AFP material
(Etched electrolytically in oxalic acid and potassium hydroxide)

CONCLUSIONS

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1) It has been shown that controlled shot peening can significantly improve threshold stresses for the initiation of HISC by as much as 10% to 15% for fine austenite spacing products, 14% for weldments and by about 5% for forged products with coarser austenite spacing's.
2) Controlled shot peening improves the HISC resistance of bar products containing chromium nitride precipitates also.
3) A post peening 2% straining, of a cross welded specimen (to simulate hydro testing) did not impair the beneficial influence of shot peening on HISC resistance.
4) The Z100 AFP forged product provides a significant increase in the HISC threshold stress, (from 85% of proof strength (for Foinaven material) to 97.5% of 0.2% proof stress) and increases in product toughness allowing application at design temperatures lower than had previously been thought possible. These HISC resistance enhancements are not currently covered by the design code but could be taken either in addition to current, possibly already conservative, design practice, or they could be built in to a strain based analysis applied at the component level to take full benefit.

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REFERENCES

1) Smith L. et al, *Corrosion Resistant Alloys for Flowlines- 30 Years Supporting Gas Production,* Proc. Conf. Offshore Materials and Corrosion: 40 Years On. Joint UK Marine Corrosion Forum and NACE, Edinburgh, UK. 20th to 22nd June 2006
2) Taylor T.S. et al, "*Foinaven Super Duplex Materials Cracking Investigation",* Offshore Technology Conference, Houston, Texas, USA. May 1999, Paper OTC 10965

3) Valdez-Vallejo, PhD. Thesis *Cathodic Hydrogen Embrittlement of Duplex Stainless Steels* University of Manchester Institute of Science and Technology. June 1990.
4) Francis R. et al, Corrosion, Volume 53, Number 3, page 234, March 1997.
5) Farrow R, *The Central Brae Pipelines,* Offshore Pipeline Technology Conference, 8th to 9th February.1990.
6) Lauvstad G.O. et al. *Improved Resistance Towards Hydrogen Induced Stress Cracking (HISC) Of Hot Isostatically Pressed (HIP) Duplex Stainless Steels Under Cathodic Protection,* Proc. Conf. NACE. Nashville, USA, 11th to 15th March 2007 Paper 497.
7) Cassagne T. and Busschaert F. *A Review on Hydrogen Embrittlement of Duplex Stainless Steels,* Proc. Conf. NACE. Bismarck USA. March 2005, Paper 5098
8) Byrne G. et.al*. Variation in the Mechanical Properties and Corrosion Resistance of Different Alloys within the Generic Designation UNS S 32760,* Proc. Conf. Stainless Steel World, Duplex 2000, Houston Texas. February 2000
9) Woollin P. et al. *Avoiding Hydrogen Induced Stress Cracking of Ferritic Austenitic Stainless Steels Under Cathodic Protection,* Proc. 23rd Int. Conf. Offshore Mechanics and Artic Engineering, Vancouver, Canada, 20-25th June 2004. Paper OMEA 2004-51203
10) Stannard D M, KBR, Private Communication
11) DNV-RP-F112, 2006. *The Design of Duplex Stainless Steel Equipment Exposed to Cathodic Protection,* Det Norske Veritas, Hovik, Norway.
12) Turbeville E, *A Summary of Recent Experiences on Designing and Fabricating Subsea Oil and Gas Production Systems with 22%Cr and 25%Cr Piping Materials,* Proc. Conf. Duplex Stainless Steels, Beaune, France October 2010, Paper II.B.3
13) Heier E.B. et al, *North Sea Failures of 13% Cr Flowlines: Consequences for Future Application,* Proc. Conf. Society for Experimental Mechanics, Costa Mesa, USA June 7th to 10th 2004.
14) EEMUA Publication 194 Edition 3, *Guidelines for Materials Selection and Corrosion Control for Subsea Oil and Gas Production Equipment,*, London UK. 2012.
15) Huizinga S. et al, *Failure of a Subsea Superduplex Manifold Hub by HISC and Implications for Design,* Proc. Conf. NACE, Grand Rapids, USA, 13th – 16th March 2006. Paper 6145
16) Byrne G. et al, *ZERON 100 AFP (UNS S 32760 Modified) Superduplex Stainless Steel for Improved Low Temperature Impact Toughness and Resistance to HISCC of API Forgings for Subsea Applications,* Offshore Technology Conference, Rio de Janeiro, Brazil. 29th to 31st October 2013. Paper OTC 13OTCB-P571-OTC
17) Mutoh Y. et al, *The Effect of Residual Stresses Induced by Shot Peening on Fatigue Crack Propagation in two Hugh Strength Aluminium Alloys,* Journal of Fatigue and Fracture of Engineering Materials and Structures. Volume 10, Issue 4, 1995 pages 261 to 272
18) Wilde BE. and Shimada ,.*Surface Modification: A Potential New Approach to Combating Hydrogen Induced Fracture in Steel,* Scripta Metal. Mater, Vol 26, pages 551 556, 1988.
19) Wilde BE. and Chattorja L, *The Effect of Shot Peening on Hydrogen Absorption by and Hydrogen Permeation Thorough AISI 4130 Steel,* Scripta Metal. Mater, Vol 26, pages 627-632, 1992
20) Al-Obaid A*, The Effect of Shot Peening on the Stress Corrosion Cracking Resistance of 2205 Duplex Stainless Steel,* Journal of Engineering Fracture Mechanics Volume 51, Issue 1, May 1995. Pages 19 to 25.
21) Iversen T.H, PhD Thesis, *Intragranular Chromium Nitride Precipitates in Duplex and Superduplex Steels,* Norwegian University of Science and Technology, NTNU- Trondheim, Norway, June 2012.
22) Pennington J, First Year PhD. Report, The University Of Sheffield, Department of Metallurgy, UK, 2015