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### **ZERON 100 (UNS S 32760 modified), Advanced Forging Process (AFP), Super Duplex Stainless Steel for Increased Low Temperature Impact Toughness and Resistance to Hydrogen Induced Stress Corrosion Cracking (HISCC) of API Forgings for Subsea Applications.**

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#### **Abstract**

As oil wells become deeper and run at higher temperatures and pressures, there becomes a need for high strength corrosion resistant material that will withstand the more severe service conditions of these projects. Over the years many projects in various locations around the world have successfully used duplex and super duplex stainless steels for subsea pipe lines, flow loops, flow lines and manifolds to contain the high temperatures and pressures and more demanding corrosive service required with the High Temperature High Pressure (HTHP) wells.

Additionally, operators have realized that they need to qualify the manufacturers of these materials following a number of problems experienced in the field. They see that the more severe conditions require a higher level of quality and security to go with the more demanding performance required. As such, the NORSOK M650 specification is seen as way to qualify the manufacturer and ensure a higher level of quality in the product. This has not solved all problems and a few operators are placing even greater demands on manufacturers to ensure manufacturers have the required metallurgical integrity to produce the more complicated alloys.

There is also a recent development for super duplex stainless steels to meet service conditions beyond usual requirements. A number of operators have projects where minimum design temperatures are calculated to be as low as  $-70^{\circ}\text{C}$ , which is near the lower shelf toughness level for duplex stainless steels. This paper discusses the properties that can be achieved by optimizing the forging route and therefore minimizing nitride precipitation in these alloys. The resultant properties are sufficient to meet the impact properties typically required at temperatures down to  $-70^{\circ}\text{C}$ . In addition, the improved ductility and toughness also increase the resistance to HISCC due to cathodic protection. Several end users and OEM's have already used ZERON<sup>®</sup> 100 AFP<sup>™</sup> to benefit from the improved toughness at design temperatures as low as  $-70^{\circ}\text{C}$ .

This paper will cover the metallurgy of duplex alloys and how improved understanding and processing can lead to less nitride precipitation, better morphology and austenite spacing that will have a beneficial effect on both toughness and HISCC resistance. The improved toughness values can also be seen across the full temperature range of most Oil & Gas projects with excellent properties at  $-50^{\circ}\text{C}$  as well as at  $-70^{\circ}\text{C}$ . Discussion of a few case histories also confirms the need for application of this Advanced Forging Process (AFP) of super duplex stainless steel.

#### **Background**

The failure of heavily cold worked super duplex stainless steel down-hole tubulars on the Marathon East Brae project confirmed the susceptibility of these alloys to hydrogen embrittlement as reported by Sentance<sup>1</sup>. After almost 20 years of successful subsea deployment of duplex and super duplex stainless steels in the solution treated condition (usually insulation coated and subject to CP potentials of around -1 Volt) the first incidence of HISCC of a super duplex stainless steel forging occurred on the BP Foinaven development in 1993<sup>2</sup>. This was quickly followed by several more cases involving forgings<sup>3, 4</sup> and pipe<sup>5</sup>. As a consequence of these failures a concerted effort was made by the industry to establish design and construction guidelines to stop HISCC. This work was initiated by The Welding Institute (TWI) resulted in Engineering Equipment and Materials Users' Association (EEUMA) guidelines<sup>6</sup>, and latterly DNV-OS-RP-F112<sup>7</sup> which is a recommended practice adopted by all deploying duplex and super duplex stainless steels subsea today. The metallurgical investigation that followed the Foinaven failure found that the material of construction fully met the specification requirements of the project. However, close examination of the forging that suffered HISCC revealed that

the ferrite grains within the forging contained chromium nitride ( $\text{Cr}_2\text{N}$ ) precipitates (Figure 1). These precipitates form in the temperature range 600 to 900°C, are needle like in shape (Figure 2), have a Hexagonal Close Packed (HCP) crystal structure<sup>8</sup> and are rich in chromium and nitrogen<sup>9</sup>. Rapid cooling from solution treatment temperatures favours precipitation of nitrides of this type and morphology as intragranular dustings within the larger ferrite grains. Isothermally formed precipitates differ in that they are cubic and decorate  $\alpha/\alpha$  grain and  $\alpha/\gamma$  grain boundaries<sup>9</sup>. At the time of the failure investigation, nothing was made of this as the material met the entire project material specification requirements. As the steel contained 25% chromium and 0.2% nitrogen, nitride precipitates were considered unavoidable. Moreover, at the time nitride precipitates were not considered to be particularly harmful to properties<sup>10</sup>. Subsequent work published Byrne et al<sup>11</sup> showed that nitride precipitates in UNS S32760 bars are detrimental to impact toughness, pitting corrosion resistance, sulphide stress corrosion cracking resistance and resistance to HISSC. It was also observed that the detrimental effect of nitride on toughness became more pronounced at lower test temperatures. Moreover, it is well recognized that the phase stability of these alloys is determined by the alloy chemistry<sup>12</sup>, such that for the same thermo-mechanical processing cycle, alloys within the same generic group can have significantly different precipitation characteristics. This is confirmed by Barbosa<sup>13</sup> who had to optimise the chemistry within the UNS S32760 designation range in order to manufacture 6" diameter forged bars and minimize nitride precipitation in the process in order to realize the quite low level specification requirements called for in NORSOK M630 MDS D57 for bar. This means that duplex and super duplex alloys must be specifically chemically formulated on the basis of achieving the desired properties. A formulation based on attainment of lowest cost while satisfying the generic UNS designation could be problematical as forge masters generally consider billet with the same UNS number will behave in the same way when processed. Recently Busschaerts et al<sup>14</sup> of Total, Turbeville<sup>15</sup> and Collie et al<sup>16</sup> both of FMC and Aursand<sup>17</sup> of Statoil have reported incidences where nitride precipitates in the ferrite phase of duplex and super duplex (UNS S 32760 and 32750 grades) have been observed in parts with lower than expected impact toughness such that the parts were either rejected or failed in service. The parts were American Petroleum Industry (API) forged flanges; induction bends, quenched off the press and forged tees respectively. It should be recognized that these parts were manufactured by NORSOK M 650 qualified mills using the qualified production routes.

Today design cases downstream of choke valves show minimum design temperatures in the range minus 60°C to minus 70°C as a consequence of Joule Thompson cooling<sup>14</sup>, these parts are also subject to cathodic protection so optimum toughness and HISSC resistance of forgings is desired. This is especially true for parts that will be joined by welding as the toughness values developed at the fusion line +2mm position can show a reduction in impact energy of between 30 to 50% of the original value measured in the parent forging.

The following pages detail the work done by the authors company to develop ZERON® 100 AFP™ that optimizes both toughness and HISSC resistance in API forgings.

## Microstructure and Phase Stability

Boonliang<sup>18</sup> took 160mm diameter ZERON 100 billet and predicted the isothermal equilibrium phase balance using the "Thermo Calc" software package over a temperature range of 400 to 1400°C. The material was cut into roughly 1cm cubes and a series of isothermal heat treatments were performed, holding at temperatures of 800, 900, 975, 1000, 1025, 1050, 1075 and 1100°C. The samples were coated in Berkatect to minimize oxidation and supported on ceramic boats inside the furnace. All heat treated samples were water quenched.

Samples from the original billet were taken in both the longitudinal and transverse directions with respect to the rolling direction of the bar. The heat treated samples were cut in half regardless of orientation. All cutting was done using a Struers Minotom cutting machine to minimize deformation. All samples were mounted in conductive Bakelite and ground to 1/4µm alumina finish, degreased with detergent, ultrasonically cleaned and rinsed in alcohol. They were then etched electrolytically using a Struers Polcontrol machine in 10 wt% oxalic acid in distilled water at a voltage of between 3 and 6 V for a period of 5 to 30 seconds. All samples were examined using optical and scanning electron microscopes.

Table 1 shows the Thermo Calc predicted phase volume fractions against the actual phase volume fractions measured in the samples. It can be seen that sigma phase is more stable at higher temperatures than predicted at the expense of ferrite and also that  $\text{Cr}_2\text{N}$  is more stable than predicted (up to 1075°C) but in smaller volume fraction than predicted. In the sample soaked at 1100°C, no nitrides were found and Thermo Calc predicted that none should be present. It can also be seen that a 1080°C solution treatment temperature provides a driving force to generate an additional 2 to 3% austenite in the structure compared to heat treatment at 1100°C. Thus in terms of development of toughness a solution treatment temperature of 1080°C was considered optimum to minimize potential for sigma formation, grain growth, and optimize the austenite content of the steel and provide a structure with a very low level of nitride precipitate.

## Toughness

A series of 5 1/8" 10k API weld neck flanges were manufactured in both ZERON 100 and ZERON 100 AFP material. The forgings were then sectioned and sets of charpy impact samples were taken from the locations shown in Figure 3. Impact testing was done at minus 50°C and minus 70°C initially. Table 2 shows the results for all sample orientations of ZERON 100 and ZERON 100 AFP forgings heat treated at 1120°C and ZERON 100 AFP forgings heat treated at 1080°C. It can be seen that reducing the test temperature from minus 50 to minus 70°C roughly halves the impact energies achieved for the same sample locations and notch orientations in the forgings. Also, it can be seen that despite a

mostly high level of toughness in the ZERON 100 forgings, when tested at minus 70°C the odd low result is realized from time to time. Metallurgical examination of samples giving low results shows them to be associated with larger than average ferrite grain structures that contained some Cr<sub>2</sub>N and some fine reformed austenite precipitates (Figure 4). In these cases there can be rafts of closely spaced austenite stringers surrounded by areas of somewhat larger austenite spacing and coarser ferrite grains. This may indicate a lack of homogeneity of deformation in the item during forging. However, moving from ZERON 100 to ZERON 100 AFP provides a significant incremental increase in toughness for all sample locations and notch orientations. Similarly, further significant increments in toughness are realized when ZERON 100 AFP material is heat treated at 1080°C. (It should be noted that in this case the 0.2% proof strength may be as low as 530 MPa compared to 550 MPa which is the specified minimum for regular ZERON 100. However, design studies using project load cases have found no material effect of a 530 MPa minimum yield, but each case needs separate evaluation). Additional toughness data with some different test temperatures is plotted in Figure 5 to try defining transition curves for each of the alloy/heat treatment condition combinations. Some overlap can be seen between the data sets but, the progressive improvements in impact toughness appear to be associated with an increase in lower shelf toughness and possibly a decrease in impact transition temperature also. ZERON 100 AFP forgings heat treated at 1080°C constitute the optimum toughness condition that meets customer requirements to address the challenges presented by Joule Thompson cooling. Some of the results obtained approach the capacity of the impact test machine even when tested at minus 70°C. Figures 6a and 6b show the development of microstructure that yields the increases in toughness. Detrimental intragranular nitride precipitates are taken into solution and transformed into beneficial intragranular precipitates of reformed austenite, which enhances toughness because of its face centered cubic crystal structure. This observation is supported by the work of Ramirez et al<sup>19</sup> who has shown that intragranular reformed austenite nucleates heterogeneously from nitrides as a consequence of low energy nitride/austenite interfaces and crystallographic compatibility.

## HISCC Resistance

Tensile specimens were sectioned from the weld neck area of the forgings, parallel to the axis of the forgings. These samples were used to measure the 0.2% proof strength and Ultimate Tensile Strength (UTS) of the forgings. Other tensile samples (Figure 7), from the same location, were taken from different planes in the forging. The grooves in the tensile sample were to facilitate the location of a linear velocity displacement transducer (LVDT) to measure the strain, as shown in Figure 8. The mounts and screws were all made of ZERON 100. The sample gauge length was surrounded by a glass vessel containing approximately 500ml of synthetic seawater. Seawater was slowly circulated through cell at a rate of about 1l/day. The potential of the sample was controlled to  $-1.035 \pm 0.005$  V SCE with a potentiostat using a platinum counter electrode and a reference electrode connected to the cell via a luggin capillary. Prior to testing, the seawater reservoir was deaerated and sodium sulphide solution was added to give a concentration of 5mg/l sulphide. This was to poison the hydrogen recombination reaction as recommended by Campbell et al<sup>20</sup>. The samples were loaded at a strain rate of  $1.0 \times 10^{-3}$ /sec up to the desired stress level. These were specific percentages of the actual yield strength of the forgings. The load was then controlled to maintain a true constant stress. After 30 days the samples were removed, cleaned in cold 10% nitric acid to remove scale (a calcareous deposit generated due to exposure to CP), and microsections were prepared to determine the presence of cracks. If no cracks were seen, the sample was ground back and re-polished so that a minimum of three complete sections were examined before freedom from cracking was confirmed. The whole of the technique employed is very similar to that used by Woollin<sup>21</sup>, so as to be able to directly compare results. These samples were also used to measure the austenite spacing of the forgings again following the method established by TWI<sup>21</sup>. The objective of this testing was to determine the threshold stress for the onset of HISCC for each of the forging types and to assess the effect austenite spacing and nitride has on HISCC resistance. Table 4 shows the raw data and Figure 9 plots the results against the original Foinavon data generated by TWI<sup>21</sup>.

Essentially, for the ZERON 100 forgings, the onset of cracking occurs at 97.5% of actual yield strength. For ZERON 100 AFP forgings, cracking begins at 100% of actual yield strength. These thresholds for cracking appear to be independent of austenite spacing over the range tested. The appearance of the cracks found is shown in Figure 10. The cracks are very fine and are found in the ferrite phase and are typically one grain deep. They are similar in appearance to the non-propagating cracks observed by Woollin<sup>21</sup>. Another common feature of these cracks is that they do not appear to pass through the austenite phase; rather they deviate in direction and go around any austenite grains in their path.

Many of the “no crack” results for both sets of forgings fall above the TWI crack/no crack criteria line. The TWI work found cracking occurred at applied nominal stresses above 87% of actual yield. This was the case for over 200 specimens including both coarse and fine austenite spacing forgings, for extruded pipes, for welds and simulated HAZ's. This indicates that the ZERON 100 and ZERON 100 AFP forgings have a higher resistance to HISCC than would be expected compared to the original Foinavon hub microstructure. This may relate to either refinement of austenite spacing or much lower nitride precipitate level or increased presence of reformed austenite or all of these factors. These factors are in fact interrelated in that finer austenite spacing's equate to shorter diffusion distances and more ready diffusion of nitrogen from the core of the ferrite grains into the adjacent austenite and consequently less nitride precipitate. Further, reformed austenite formation would be expected to toughen the matrix and provide high solubility/low diffusivity sinks for hydrogen gas. Further, previous work<sup>11</sup> using slow strain rate testing of nitride and non-nitride burdened material showed that the presence of nitrides reduced the resistance to HISCC (as measured by plastic strain ratio in slow strain rate tests) by as much as 40%. Other workers<sup>22</sup> have argued that because of differences in coherency between the ferrite crystallographic planes and the sides and tips of nitride precipitates, the tip of these nitride precipitates could act as sinks

for hydrogen and maybe preferential sites for initiation of hydrogen cracking and this could promote crack propagation on {OOI} cleavage planes in ferrite on which the precipitates are located. The authors provide orientation relationship measurements between the nitride precipitates and the ferrite cleavage planes to support this theory. So our production methods substitute detrimental nitrides with beneficial reformed austenite. This benefits both toughness and HISSC resistance.

However, the ZERON 100 AFP forgings showed the highest threshold for the onset of HISSC. As can be seen in Figure 9, about 80% of the ZERON 100 AFP austenite spacing's measured were below 40 microns whereas only 12% of the ZERON 100 austenite spacing's measured was below 40 microns. It is important to note that the TWI method of measurement of austenite spacing was followed, this means reformed austenite within the ferrite grains was ignored and only distances between primary austenite bands were measured. These tests showed no influence of spacing on threshold stress for cracking over the range of spacing's tested. The performance of ZERON 100 AFP material suggests that the "coarse grain" allowable stress de-rating applied in DNV F112 may be overly conservative for this product.

## Summary

Proprietary incremental metallurgical changes in alloy chemistry, forging method and heat treatment practice have led to the development of ZERON 100 AFP. This grade has enhanced low temperature impact toughness and better resistance to HISSC when subject to cathodic protection in subsea applications. The alloy is capable of providing high levels of toughness measured in several locations and with several notch orientations at temperatures as low as minus 70°C, such that leak before break impact toughness requirements are met. Weld procedure qualifications have confirmed that very adequate levels of toughness are retained at the fusion line, fusion line +2 positions also. To date 4 subsea projects have utilised this solution in cases where Joule Thompson cooling effects are encountered and have benefited from the excellent levels of toughness realised.

It is well known that metallurgical changes that improve toughness also usually come with a corresponding improvement in resistance to hydrogen embrittlement<sup>23</sup>. This is the case with ZERON 100 AFP. Threshold stresses for HISSC are 97.5% of actual yield, a significant increase in threshold when compared to the 87% defined by TWI. Of course DNV – RP- F112 design criteria are based upon materials that exhibit the 87% threshold stress. So, this crack resistance enhancement can either be taken as an additional factor of safety over and above that provided by F112 with the F112 allowable stress de-rating for coarse grain material being applied or there may be an argument to consider that only the fine grain size de-rating factor should be applied for this grade of forging. The levels of toughness and HISSC resistance achieved allow engineers to be able to specify ZERON 100 AFP for applications where Joule Thompson cooling may occur or indeed when and where a general higher level of integrity is preferred, be that topside or subsea.

## Conclusions

1. The ZERON 100 AFP grade is derived from proprietary changes in chemistry, forging schedule and heat treatment.
2. Impact toughness tests made on samples taken from various locations and with various notch orientations, within actual API 5 1/8" 10k weld neck forgings, have shown excellent levels of toughness at low test temperatures, such that impact levels currently required at minus 50°C can be achieved at minus 70°C.
3. The impact toughness provided makes ZERON 100 AFP a strong materials selection candidate for situations involving Joule Thompson cooling, for parts in critical applications or indeed for customers generally requiring the highest integrity product available, be this for subsea production or topside. As many operators are now moving to strengthen their specification requirements for duplex stainless steels ZERON 100 AFP becomes an ideal solution.
4. Toughness enhancements have also had the knock on effect of providing improvement in resistance to hydrogen induced stress corrosion cracking as a consequence of cathodic protection. Threshold stresses for cracking have been increased from 87% of actual yield strength to 97.5% of actual yield strength. This improvement may be considered either as an additional margin of safety or could be taken to argue that the allowable stress de-rating applied to items with a coarse austenite spacing (above 30 microns) by DNV- RP- F112 need not be applied. In fact the threshold stress levels measured in this work appear to be independent of austenite spacing for the range of spacing's tested.
5. The improved properties correlate with microstructures with finer austenite spacing's, low levels of chromium nitride precipitates and high levels of intragranular reformed austenite. The reformed austenite is inherently tough and it has a high solubility for hydrogen gas and a low diffusivity of the gas once in solution so any hydrogen absorbed stays there. The substitution of nitride with reformed austenite brings big rewards since the detrimental effect of the nitride is lost and is replaced with the beneficial effect of reformed austenite.

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**Table 1: Measured vs predicted volume fractions of phase**

Sample	Measured Volume Fraction (%)				Predicted Volume Fraction (%)			
°C	Ferrite	Austenite	σ Phase	Cr <sub>2</sub> N	Ferrite	Austenite	σ Phase	Cr <sub>2</sub> N
800	-	69.627	30.373	-	-	67.187	30.719	2.094
900	-	73.638	26.362	-	11.442	68.048	18.941	1.569
975	34.76	41.710	23.530	-	43.067	56.007	-	0.926
1000	45.55	42.670	11.780	0.00987	41.875	57.625	-	0.500
1025	n/m	n/m	n/m	0.00449	40.599	59.401	-	-
1050	n/m	n/m	n/m	0.00159	42.687	57.313	-	-
1075	n/m	n/m	n/m	0.00064	45.000	55.000	-	-
1100	n/m	n/m	n/m	-	47.538	52.462	-	-

Note: n/m = Not Measured

**Table 2: Charpy impact test results**

Test Temp °C	Position	ZERON 100		ZERON 100 AFP		ZERON 100 AFP	
		Solution Treated at 1120°C		Solution Treated at 1120°C		Solution Treated at 1080°C	
		Result (J)	Avg (J)	Result (J)	Avg (J)	Result (J)	Avg (J)
-50	CT BODY	110	100	130	119	180	194
-50	CT BODY	100		116		196	
-50	CT BODY	90		111		150	
-50	CL BODY	101	106	251	242	213	239
-50	CL BODY	100		264		258	
-50	CL BODY	118		212		142	
-50	CL NECK	143	117	244	228	221	210
-50	CL NECK	108		216		262	
-50	CL NECK	102		224		191	
-70	CT BODY	34	34	74	59	129	127
-70	CT BODY	36		57		140	
-70	CT BODY	34		46		114	
-70	CL BODY	52	60	77	121	92	157
-70	CL BODY	64		188		183	
-70	CL BODY	66		98		197	
-70	CL NECK	35	55	89	69	92	93
-70	CL NECK	76		64		67	
-70	CL NECK	56		54		119	

**Table 3: Charpy Impact Transition Temperature Test Results**

Charpy Impact Energy (Joules)

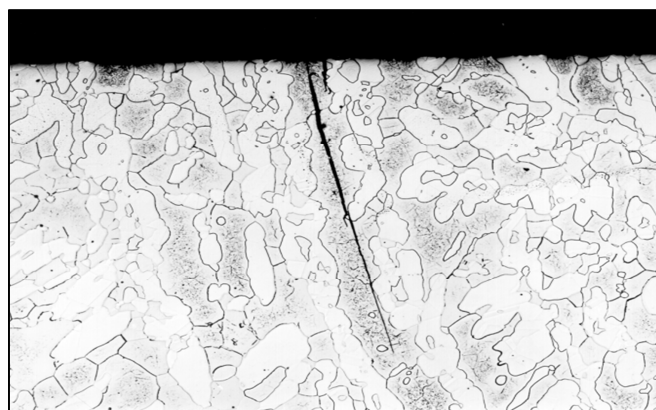
Test Temp °C	ZERON 100 - Annealed 1120°C	ZERON 100 - Annealed 1080°C	ZERON 100 AFP - Annealed 1120°C	ZERON 100 AFP - Annealed 1080°C
-80	22		51	
-80	27		68	
-70	50	41	92	127
-70	29	83	102	157
-70	34	69	59	93
-70	60		121	
-70	55		69	
-60	65		129	
-60	74		155	
-50	100	133	242	194
-50	106	192	119	239
-50	107	212	228	210

**Table 4: HISCC Test Results and Austenite Spacings**

Forging ID	PRODUCT FORM	STRESS RATIO (%)	AUST. SPACING (µm)	CRACK/ NO CRACK
T1223	ZERON 100 Forging	100	42	C
		95	43	NC
		90	42	NC
T1375	ZERON 100 Forging	100	46	C
		95	45	NC
		90	44	NC
T1955	ZERON 100 Forging	100	48	C
		95	48	NC
T3416	ZERON 100 Forging	100	45	C
		100	54	C
		97.5	50	C
		97.5	51	C
		95	46	NC
		95	56	NC
T5063	ZERON 100 Forging	100	20.8	C
T5496	ZERON 100 Forging	105	28	C
		100	28	C
		100	28	NC
T4375	ZERON 100 Forging	100	28.19	C
T4374	ZERON 100 AFP	110	31	C

	Forging	105 100	39 38	NC NC
T4766	ZERON 100 AFP Forging	105 100 97.5 97.5 97.5	51 40 46 36 52	C C NC NC NC
T5033	ZERON 100 AFP Forging	100	46.59	NC
T5378	ZERON 100 AFP Forging	100	37.28	NC
T5495	ZERON 100 AFP Forging	105 100 100	33 27 33	C C NC
T5794	ZERON 100 AFP Forging	100 97.5 95	39.5 40.3 32.5	NC NC NC
T5795	ZERON 100 AFP Forging	100 97.5 95	37.59 28.32 26.87	C NC NC

**Figure 1: Cracking observed in the Foinaven hub forgings**



**Figure 2: TEM examination of extraction replica showing nitride precipitate needles**





Figure 3a and 3b: Location of impact samples in the forgings (after Shell)

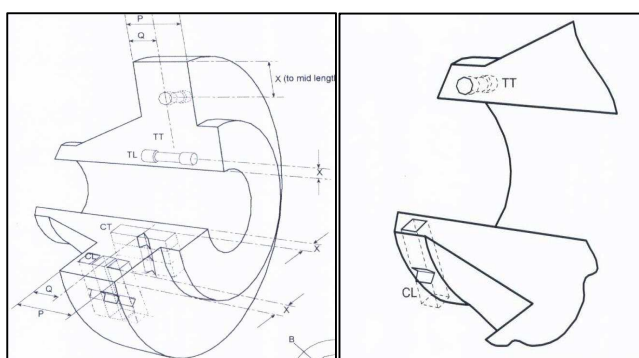


Figure 4: Microstructure associated with a Charpy impact sample with lower impact energy

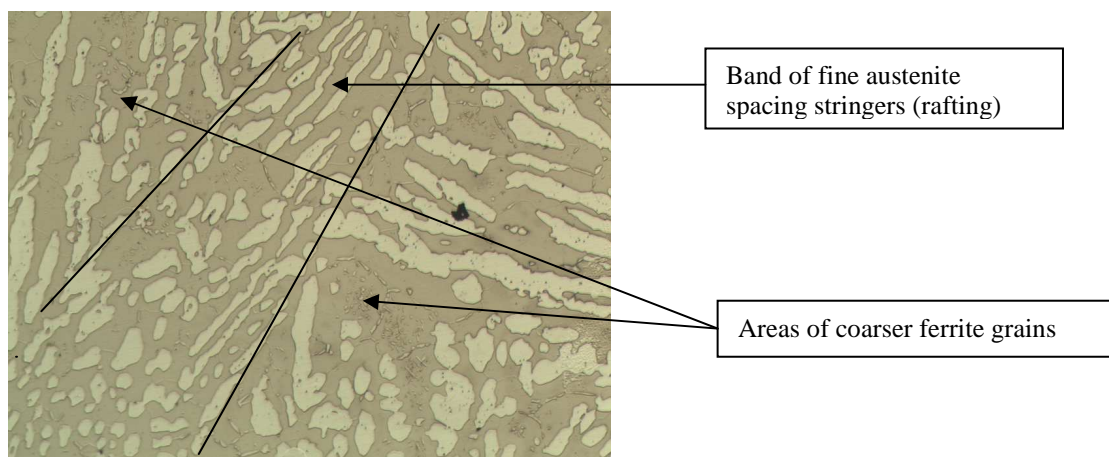


Figure 5: Charpy Impact Test Transition Curves

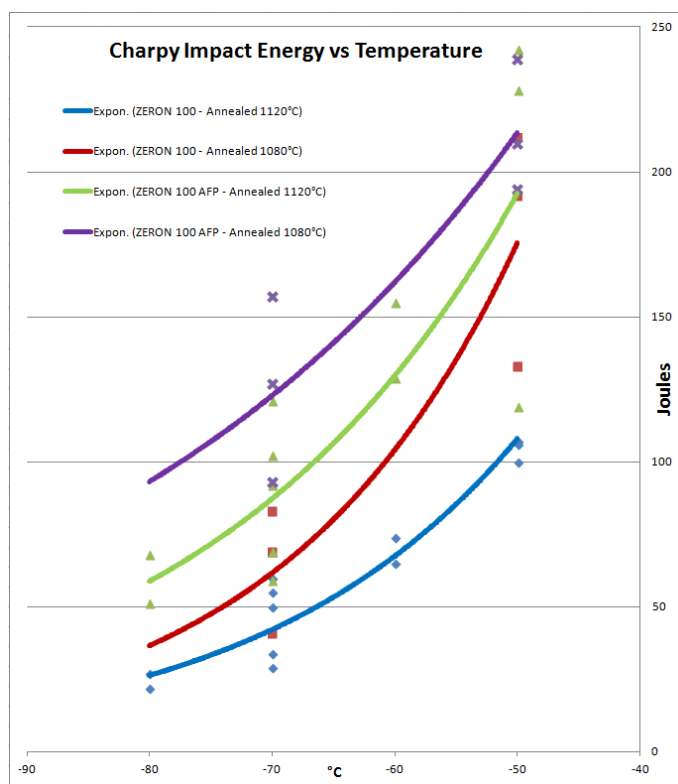


Figure 6a ZERON 100 (1120), nitrided forging and 6b ZERON 100 AFP (1080): microstructures

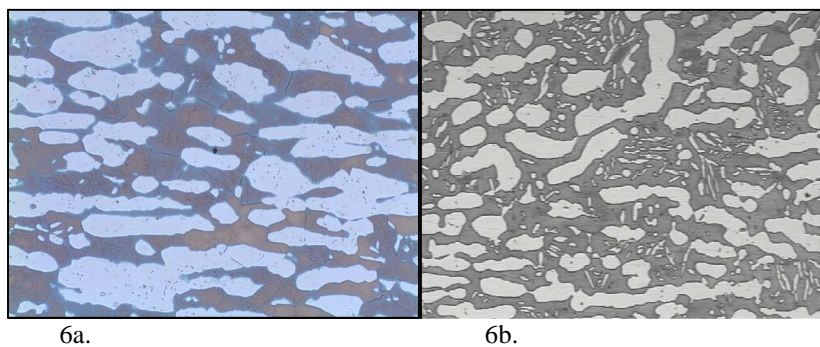


FIGURE 7: Drawing of hydrogen embrittlement test sample.

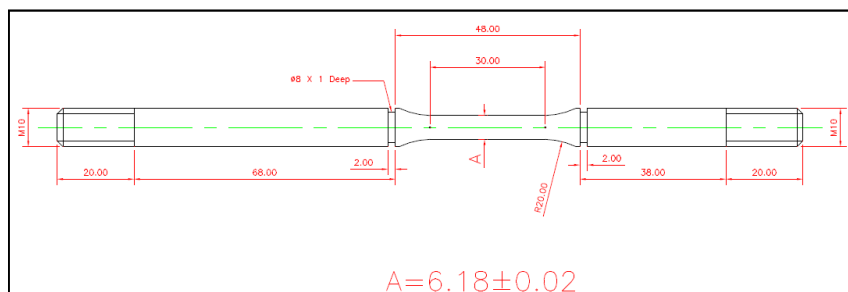


FIGURE 8: Appearance of sample with LVD transducer in place

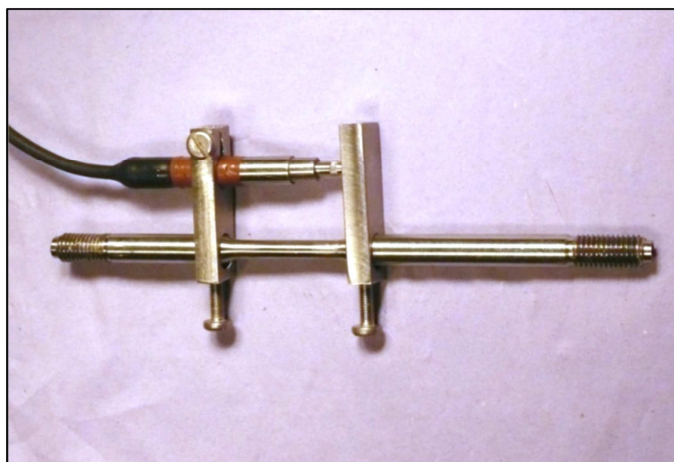


Figure 9: Threshold stress for cracking vs austenite spacing showing the TWI curve based on Foinaven, ZERON 100 and ZERON 100 AFP data in seawater at -1.04V SCE.

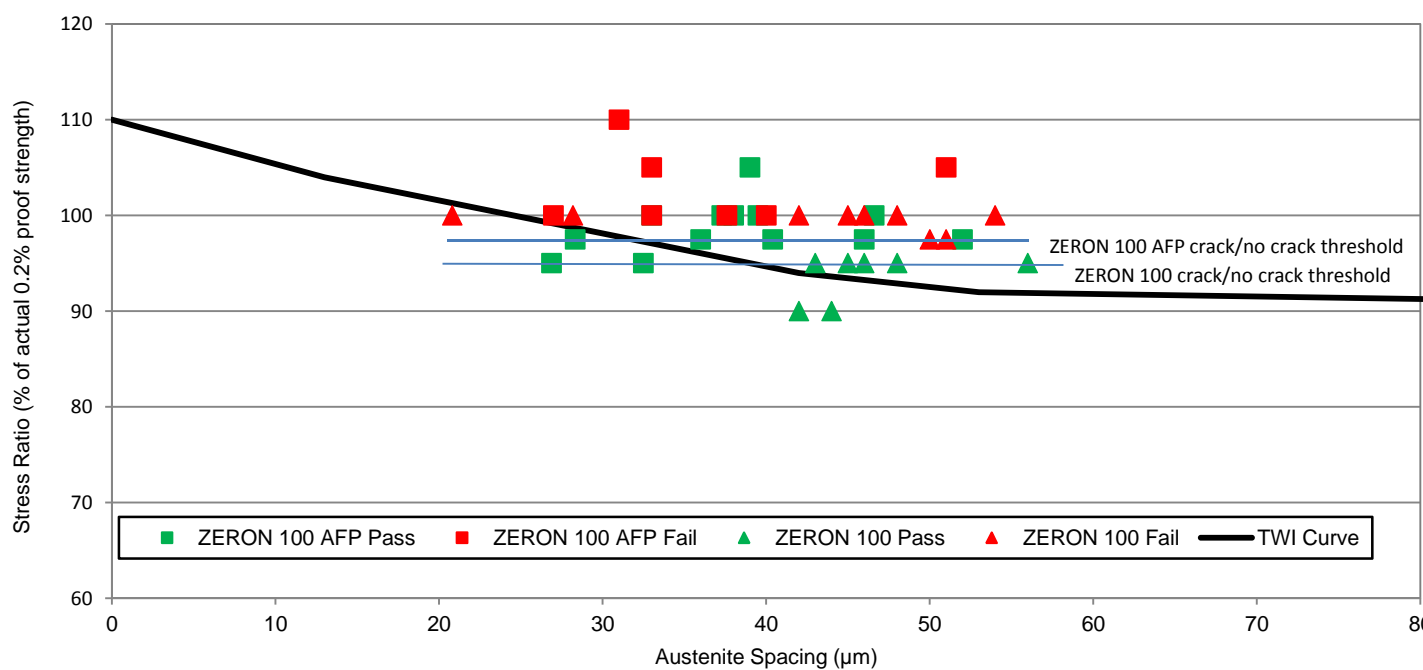


Figure 10: The appearance of HISSC

