The Threshold Stress for Initiation of Hydrogen Embrittlement in Various Product Forms of Z100 Superduplex Stainless Steel

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Summary

Duplex and superduplex stainless steels have been used for many years for subsea components by the oil and gas industry. Because carbon steel is invariably also present, these structures are cathodically protected, usually with zinc or aluminium anodes. At these anode potentials, hydrogen is evolved as part of the cathodic reaction, but generally this has caused no embrittlement problems with the many thousands of tonnes of duplex and superduplex stainless steel that are installed subsea.

However, a small number of failures of highly stressed components has focused attention on the appropriate design stresses and permissible strains for duplex alloys with CP. Work on the first failure suggested a design stress of 80% of the 0.2% proof stress and a maximum of 0.5% strain. This data was obtained from a very large forging with a coarse microstructure, which is not typical of the pipes, fittings and flanges that are also used subsea. Tests under constant load have been conducted on a range of Z100 superduplex stainless steel components commonly used in subsea structures. The results show that much higher design stresses and maximum strains can be utilized safely without risk of embrittlement for components in common subsea use. The metallurgical constraints are discussed.

Keywords

Superduplex stainless steel, hydrogen embrittlement, threshold stress, austenite spacing.

Introduction

Over the last few years there have been several failures of duplex and superduplex components subsea due to hydrogen embrittlement. The hydrogen is produced as the cathodic reaction by the CP system on the subsea structure. All of the failures were associated with local high stresses. Concern was expressed about the adequacy of design rules at the time and new recommendations were made to avoid hydrogen embrittlement of cathodically protected duplex stainless steels used subsea [1, 2]. It is recommended that design conditions be used such that low temperature creep (plastic deformation) is avoided. The work of Woollin et al [3] suggested a limit of 80% of actual 0.2% proof stress or 0.5% of total strain. However, these recommendations were based on material from the Foinaven failure [4], which was somewhat unusual in that the orientation of the structure at the failure site was at right angles to that normally expected, due to design constraints. The ferrite content was also at the high end of the permitted range. Woollin et al [3] showed that both these factors increase the propensity for hydrogen embrittlement.

The present work was undertaken to determine the threshold stress and strain for Zeron 100 (Z100) superduplex stainless steel product forms typical of those used in subsea wellheads.

Experimental

Materials

Zeron 100 pipes fittings and flanges have been used for Subsea completions since 1995. A review of Zeron 100 supply for subsea completions over 2004/5 by Weir Materials showed that the most common product forms with heavy sections were NPS6 Schedule XXS pipe and $5^{1}/_{8}$", 10,000lb flanges. NPS 6 schedule XXS elbows and tees were also supplied, but as these are manufactured from pipe, it was considered that testing of the pipe would be satisfactory initially. A length of pipe from current production was selected for testing.

Black forgings for $5^{1}/_{8}$", 10,000lb flanges are routinely manufactured and they typically have a spread of properties. Three forgings made from different casts were selected for testing. The materials were:-

A - NPS6 schedule XXS pipe
B1 - $5^{1}/_{8}$", 10,000lb flange forging
B2 - $5^{1}/_{8}$", 10,000lb flange forging
B3 - $5^{1}/_{8}$", 10,000lb flange forging

Metallography

Metallographic sections were prepared of all the materials. Samples were taken from several different parts of the forgings at the mid radius position to determine what changes in microstructure might have occurred. The phase balance was measured by a computer controlled image analysis technique and the austenite spacing was measured using the TWI recommended procedure [5].

Hydrogen Embrittlement Testing

Tensile samples were machined from each material as shown in Figure 1. The grooves in the sample were to facilitate the location of an linear velocity displacement transducer (LVDT) to measure the strain, as shown in Figure 2. 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/d.

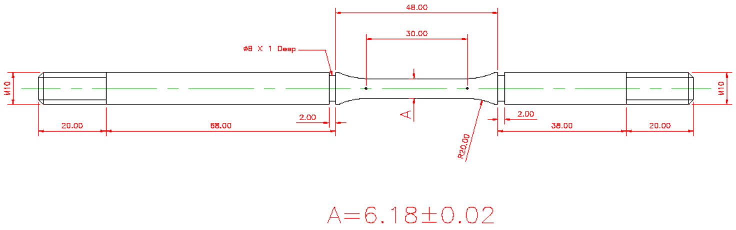

FIGURE 1 Drawing of hydrogen embrittlement test sample.

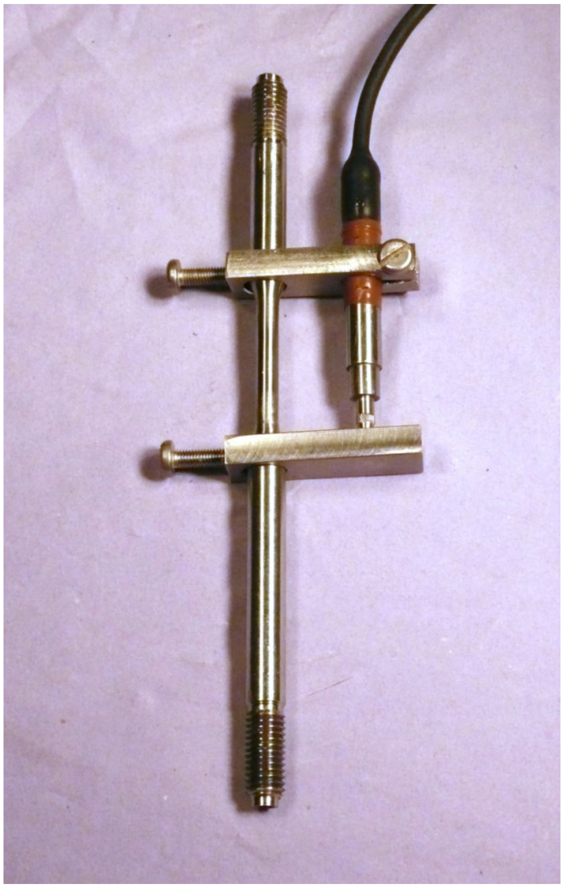

FIGURE 2 Appearance of sample with LVD transducer in place

The potential of the sample was controlled to –1.035 ± 0.005 V SCE with a potentionstat 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 [6].

The samples were loaded at a strain rate of 1.0 x 10^{-3}/sec up to the desired stress. 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, 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 [3], so as to be able to directly compare results.

Results and Discussion

Metallography

The results for all the samples are shown in Table 1. Note that the Charpy impact energy was measured at -70°C, rather than the more common -50°C. The lower temperature is becoming common for subsea wellheads and Weir Materials regularly tests materials at this temperature. The three different forgings were selected because of the range of Charpy impact energies that were seen. However, the 0.2% proof stresses, ferrite contents and austenite spacings were all similar.

Table 1. *Properties of materials tested.*

SAMPLE	**FORM**	**0.2% Proof Stress (MPa)**	**Charpy Energy @ -70°C (J)**	**Ferrite (%)**	**Austenite Spacing (µm)**		
					Min	**Mean**	**Max**
A	6” XXS	636	100, 105, 126	52.4	14	19	26
B1	$5^1/_8$” 10Klb Forging	595	288, 294, 296	51.8	38	42	46
B2	$5^1/_8$” 10Klb Forging	575	65, 76, 82	54.3	41	46	50
B3	$5^1/_8$” 10Klb Forging	583	138, 138, 142	54.9	45	47	50

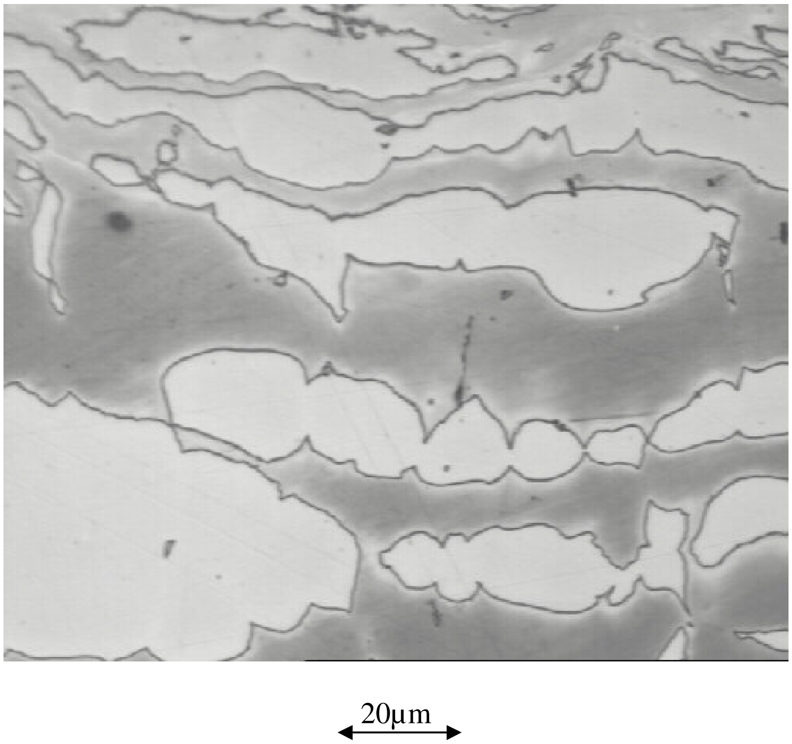

FIGURE 3 Microsection of 6” XXS pipe.

Figure 3 shows a typical microstructure for the NPS 6 pipe, while Figure 4 shows the microstructure of forging B3. The microstructures of B1 and B2 were very similar. Figure 3 shows a typical pipe microstructure with elongated laths of austenite in a ferrite matrix, which is more or less uniform across the whole thickness. Figure 4 shows the variability of the forged microstructure. It consists essentially of large laths of austenite in a ferrite matrix with smaller austenite laths in between. The reason for this is that forging is typically carried out at around 1200°C where the phase balance is strongly ferritic. After forging, the material is solution annealed at 1120±20°C, where the smaller austenite particles can precipitate from the ferrite, hence the term, reformed austenite. When measuring the austenite spacing, the TWI method requires ignoring all smaller austenite particles.

Figure 4 shows the directionality of the forged structure at various locations. At position 1, the directionality of the starting billet is clearly evident. At position 2, the austenite laths are somewhat shorter and show directionality around the corner of the forging. In position 3 a lot of the directionality has been lost, as a result of forging. In positions 4 and 5 the directionality is now parallel to the radius of the flange and the axis respectively, as a result of the forging operation. The gauge length of the tensile samples was in region 2, near to the outside surface.

Table 2 shows the variation in phase balance and austenite spacing at the same positions as the microsections in Figure 4. The results show that the mean ferrite content was remarkably consistent in all five regions, as was the mean austenite spacing.

Table 2. Phase balance and austenite spacing for the forging shown in Figure 4.

	Ferrite (%)			**Austenite Spacing (µm)**		
POSITION	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**
1	50	55.2	61	44	50	57
2	43	54.9	61	45	47	50
3	47	53.8	58	46	53	64
4	52	55.3	59	41	48	58
5	47	54.7	59	45	50	56

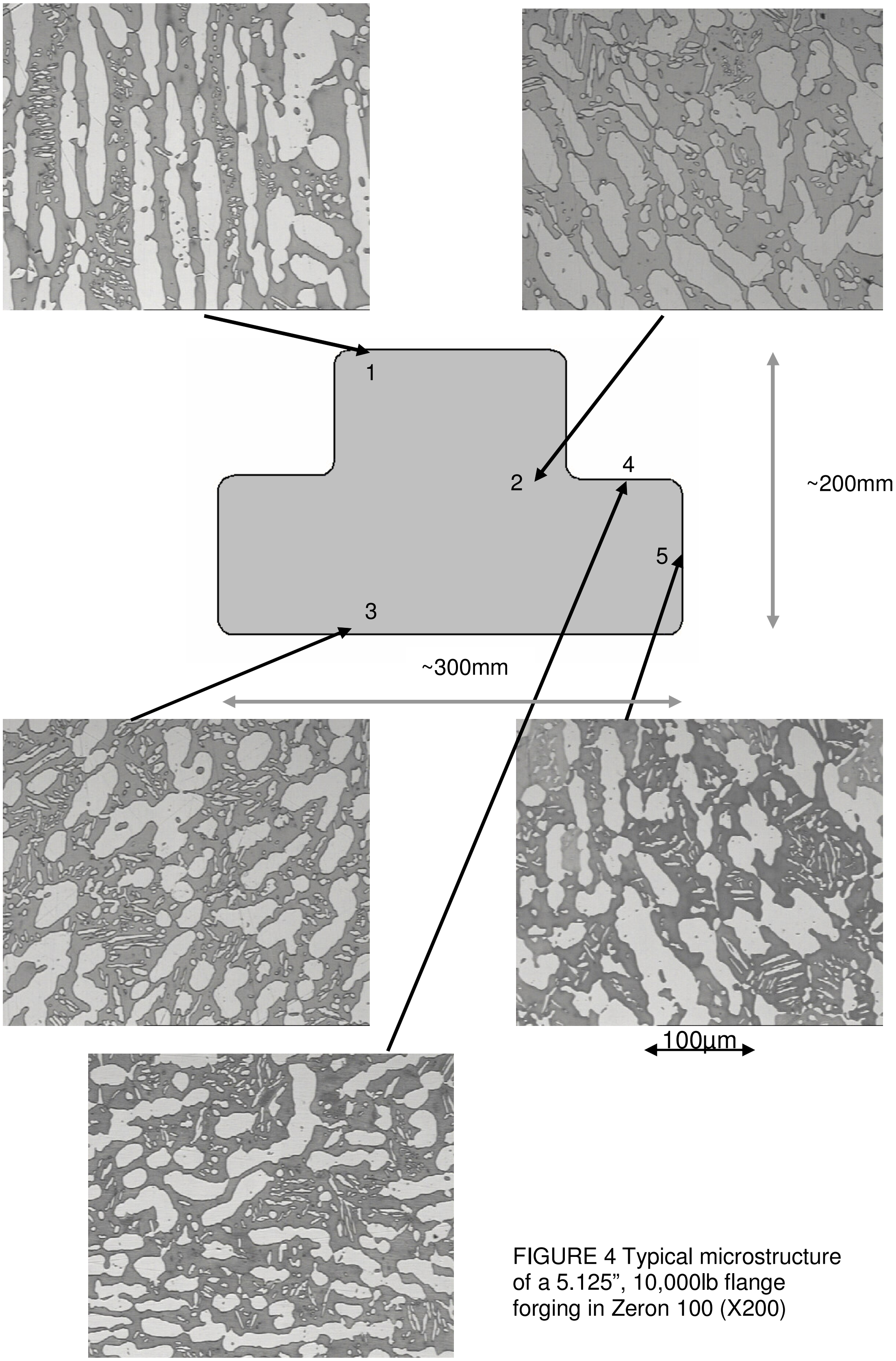

FIGURE 4 Typical microstructure of a 5.125”, 10,000lb flange forging in Zeron 100 (X200)

Hydrogen Embrittlement Tests

When hydrogen embrittlement cracking was seen it was typically as shown in Figure 5. There were usually only a couple of cracks visible in a single microsection and these varied in length from about 10 to 60µm. These small cracks are assumed to be non-propagating cracks, as defined by Woollin[5]. He showed that short cracks are the same length after 24 hours as they are after 720 hours. They clearly initiate early on when the rate of straining is high, but they do not propagate when the rate of straining decreases. When the stress is further increased, these cracks can then propagate. The non propagating nature of the cracks will be checked in future work.

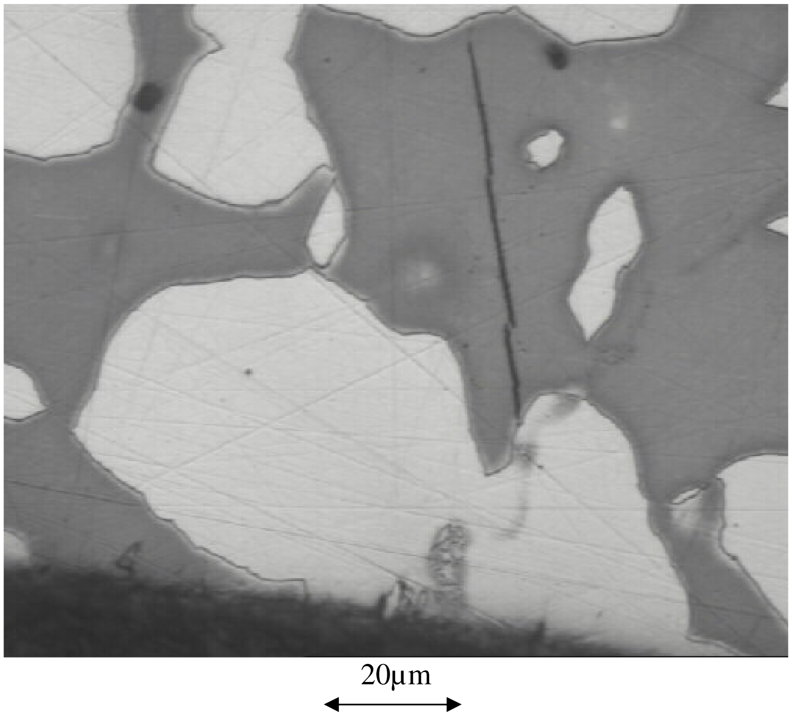

FIGURE 5 Microsection showing crack in forging B1 at 100% of proof stress.

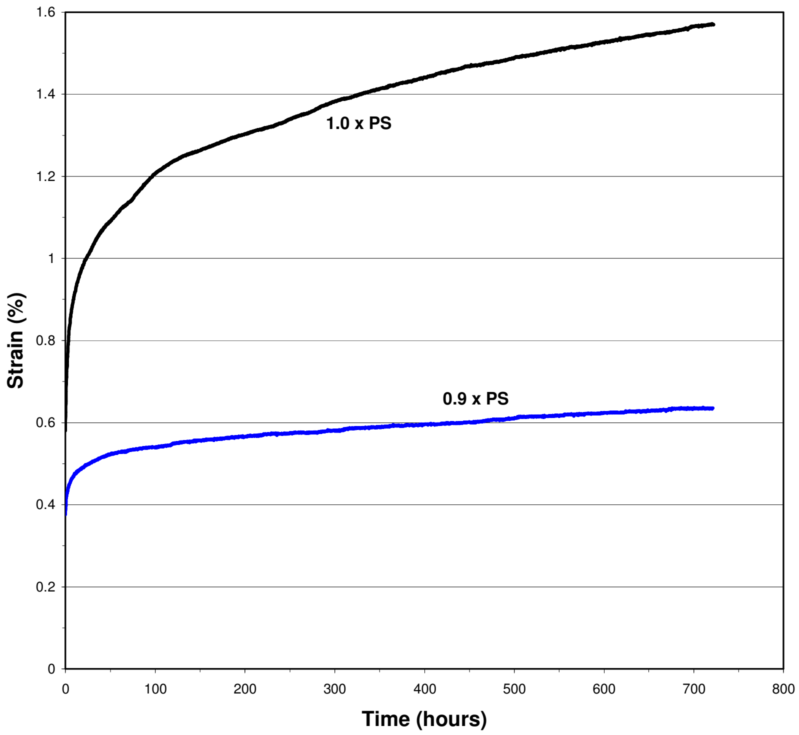

FIGURE 6 Strain versus time for forging B1.

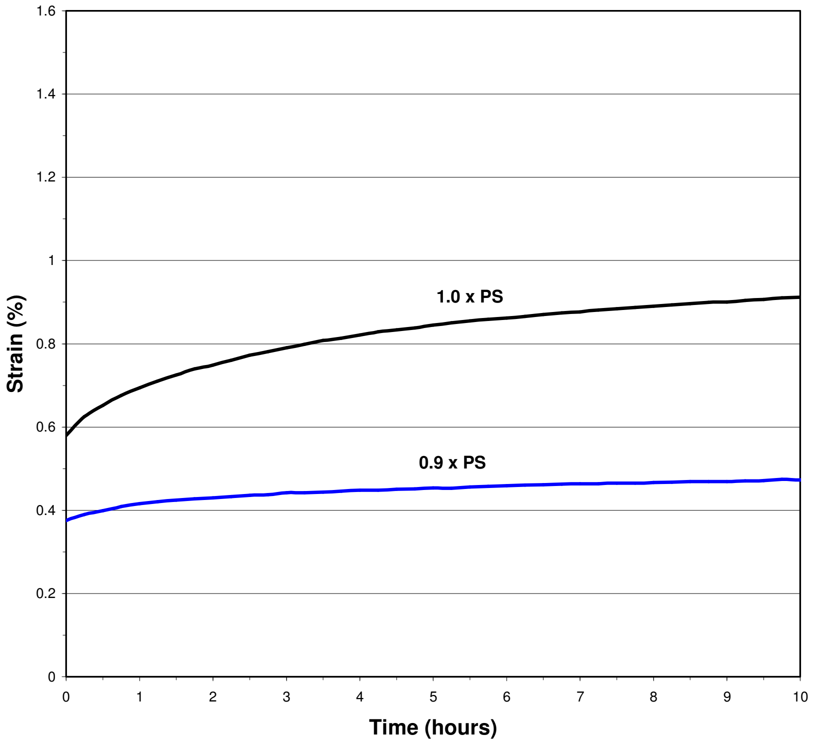

FIGURE 7 Strain versus time for forging B1 (first 10 hours).

Table 3 shows the results from the hydrogen embrittlement tests to date and testing to fill in the blanks continues. The results show that stresses up to 90% of the actual 0.2% proof stress do not lead to hydrogen embrittlement cracks for the heavy section products tested. What is also of interest is the threshold strain for crack initiation. Figure 6 shows the typical change of strain over a 720 hour test. Figure 7 shows that 50% of the strain has developed in the first 5 to 10 hours. When the rest of the data is available it may well be possible to relate the strain after a few hours to the likelihood of hydrogen embrittlement cracks developing. From the data in Table 3, it is clear that strains up to 0.94% do not cause cracks in the materials tested to date.

The results of Woollin[3, 5] suggested a maximum austenite spacing of 30µm to prevent hydrogen embrittlement crack initiation at stress around the 0.2% proof stress. The results of the present tests on large forgings, with a spacing of around 45µm, suggest that this figure should be reexamined. In the TWI method for measuring austenite spacing all reformed austenite islands are ignored. Unfortunately the critical size of these islands is not defined and the microsections in Figure 4 show that some of the reformed austenite islands are quite large. With a re-definition of what size of austenite can be accepted, the austenite spacing of the forgings in the present tests could be much lower. This would then bring the present results more into line with those of Woollin [3]. The results of these tests on materials routinely used subsea with cathodic protection give confidence that total stresses up to 90% of the 0.2% proof stress will not result in hydrogen embrittlement cracks under cathodic protection and even higher stresses may be possible when the work is complete.

Table 3. Results of Hydrogen Embrittlement Tests

STRESS	**Strain after 30d (%)**			
	6” XXS Pipe	**5$^{1}/_{8}$” ; 10,000lb Forgings**		
(% of PS)		**B1**	**B2**	**B3**
110	🟥 2.24			
100	🟩 0.67	🟥 1.57		🟥 2.03
95		🟩 1.35	🟩 0.94	🟩 0.42
90		🟩 0.64	🟩 0.56	

🟥 = Cracks

🟩 = No Cracks

Conclusions

1. Hydrogen embrittlement tests have been conducted on thick wall pipe and $5^1/_8$", 10,000lb forgings in seawater at -1.04V SCE.

2. An examination of the microstructure of the forgings shows the phase balance and austenite spacing to be more or less constant throughout the forging and only the directionality of the austenite changes.

3. No embrittlement cracks have been seen on any of the materials tested to date up to 95% of the 0.2% proof stress.

4. The results for the forgings suggest that the TWI definition of ignorable austenite, when determining the austenitic spacing, needs to be re-examined, perhaps based on size of the austenite particle.

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