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The Effect of Post Weld Surface Treatments on the Corrosion Resistance of Super Duplex Stainless Steel Welds in Sea Water

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ABSTRACT

Super duplex stainless steel sea water piping systems have been in use since 1991, generally with excellent results. However, there have been one or two problems at start-up for a few projects and a number of post weld surface treatments have been proposed to improve service performance. The paper describes the results of laboratory tests to investigate the effects of some of the treatments that have been suggested. Some of these offered a substantial improvement to the critical pitting temperature, and the practicality of these is discussed in relation to service experience.

Keywords: Sea water, stainless steel, welding, pitting

INTRODUCTION

Super duplex stainless steel has been used for sea water and firewater piping systems since 1991. These have largely been of welded construction and only a few problems have been reported (1).

The problems that have occurred with welds are mostly due to poor design or incorrect fabrication (2). The temperature limit to which welds can be used in sea water is not known and the results are not consistent. One offshore platform has operated sea water discharge piping at 65°C for over two years with no problems. Another platform suffered corrosion at welds soon after start up with a sea water discharge temperature of 45° to 50°C, while there had been no problems in the cooler parts of the sea water system.

It has been suggested that a slow start up regime improves the performance of stainless steel in sea water (3), and it may be noted that the platform operating at a discharge temperature of 65°C had a very gentle start up (1).

Other people have suggested that the surface film is not stable and needs passivating prior to entering service. A further suggestion has been that welds should be pickled after welding to remove "deleterious" surface layers.

The present work was undertaken to investigate the effects of a variety of surface finishes on the pitting temperature of super duplex stainless steel welds in sea water.

EXPERIMENTAL

Materials

6 pieces of 4mm thick Zeron 100 * super duplex stainless steel plate (cast S33019) were cut 300mm x 100mm. Two of these were welded together by GTAW using Zeron 100X *consumables to give a weld approximately 300mm long. This was welded with 2.4mm diameter wire in 2 passes with low heat inputs (<1kJ/mm) and low interpass temperatures (<70°C).

The remaining plates were welded together by SMAW using similar coated welding consumables to give 2 further welds approximately 300mm long. These were welded in a single pass with 3.4mm electrodes at low heat input (<1kJ/mm).

The welds were designated as follows:

OC8511/A - GTA weld

OC8511/B - SMA weld

OC8511/C - SMA weld

All the welds were thoroughly wire brushed with a manual stainless steel brush.

The samples cut out of each plate for the laboratory tests were 60mm x 12mm x 4mm with the welds across the centre. The cut edges were ground to 240 grit SiC, and the sharp edges were beveled. A 200mm 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 duramastic

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lacquer to prevent their wetting by sea water.

Microsections of each weld showed a two-phase microstructure in the weld with ferrite contents in the range 50% to 60%. A small quantity of sigma phase was seen in the HAZ of all the welds. This is typical of thin wall super duplex welds. The sigma precipitates were not continuous, and were less than 1% in all locations. This is well below the concentration required to form a continuous network of depleted zones that can reduce corrosion resistance (4).

Corrosion Tests

<u>ASTM G48 Method A</u>

Samples of all three welds were tested according to ASTM G48 Method A in ferric chloride solution. The initial exposure was at 30°C for 24 hours. Subsequent exposures were for 24 hrs at increasing temperature in increments of 5°C until a substantial weight loss occurred.

<u>Sea Water</u>

Electrochemical tests were carried out in glass vessels of capacity 750ml. These were filled with synthetic sea water made as follows:

$NaCl$	-	28g/l
$Mg\ SO_4.9H_2O$	-	7.74g/l
$Mg\ Cl_2.\ 6H_2O$	-	6.02g/l
$Ca\ Cl_2.\ 6H_2O$	-	2.27g/l
$Na\ HCO_3$	-	0.2g/l

pH 7.8 – 8.2 (adjusted with NaOH).

Compressed air was continuously bubbled through the sea water and the specimens were mounted so that the water line was 10 to 15 mm below the upper plate edge. This meant that the weld, both HAZ's and some parent metal were immersed. The total surface area under water was
~ $16cm^2$.

The potential was allowed to stabilise for about 15 minutes. The samples were then gradually polarised to +600 mV SCE over 30 minutes, as this is the potential of high alloy stainless steel in chlorinated sea water (5,6). The current was then allowed to stabilise for two hours at room temperature, after which the temperature was increased at 5°C/hour up to ~ 80°C where it was allowed to remain for two hours. The current and temperature were monitored continuously throughout the test.

Some samples received a pre-treatment prior to testing. This involved either some kind of exposure in aerated sea water, or a chemical treatment of the sample surface.

After testing the samples were washed, dried and examined under a microscope for indications of corrosion.

Pretreatment

From the introduction it can be seen that a number of pretreatments could be considered for welds. Three were chosen for investigation as follows:

1) Polarised to +600 mV SCE in sea water for two weeks at room temperature.

2) Passivated in 20 vol % nitric acid for 20 minutes at room temperature.

3) Pickled in 20 vol % nitric acid plus 4 vol % hydrofluoric acid at 55°C for 2 hours.

As-welded, wire brushed samples were used for reference purposes.

The samples treated by method 1) were transferred immediately to the test cells for critical pitting temperature (CPT) determination. Welds treated by method 2) were washed in distilled water. Samples treated by method 3) were also washed in distilled water and were then allowed to passivate in air for 24 hours. The reason for this is that although method 3) is sometimes called a pickle and passivation treatment, it only pickles the sample and passivation of the surface must follow separately.

RESULTS AND DISCUSSION

ASTM G48 Method A

The results of the ferric chloride critical pitting temperature tests are shown in Table 1. All of the samples showed pitting in the weld metal, usually on both the cap and root. One surprising result is that the SMA welds performed a little better than the GTA welds. The latter welds had more heat tint than the SMA welds, which had no residual flux deposits after wire brushing. The pitting in the GTA welds may have been due to the heat tint acting as a shield, and thus creating some kind of local occluded cell. The higher weight loss at 30°C on all the samples is probably due to the acidic test solution cleaning up the surface. A weight loss exceeding 20mg would be indicative of pitting. No pitting was observed, even after using a pointed steel probe, in any samples after testing at 30°C. These results are typical for good quality super duplex welds.

Sea Water

Figure 1 shows a typical current vs time trace for a welded sample. The temperature vs time trace is included for clarity. Pitting is usually said to have initiated when the current density exceeds 10μ A/cm^2 (7), when the passive current density is less than 1μA/cm^2. The current density on a few specimens did not drop below 1μA/cm^2 before starting to increase the temperature, even after leaving them for 2 or 3 hours. A typical example is shown in figure 2.

In this case pitting was deemed to have initiated when the current density exceeded ten times the mean steady current density at ambient temperature.

The results of the CPT tests are shown in Table 2. All corrosion was on the weld metal on all samples. The CPT results in sea water for as-welded material are not as high as those in the ferric chloride test. The potential of super duplex stainless steel in 6% ferric chloride is about +600 mV SCE, the same as used in the sea water tests. However, the pH of ferric chloride solution is about 1.5, much more acidic than the synthetic sea water. The ferric chloride probably cleans up the surface of welds in a manner similar to the pickling and passivating solutions described below, which also resulted in increased CPT values.

The current/time plot for a typical sample during pre-exposure in aerated sea water at +600 mV SCE is shown in Figure 3. It can be seen that the current decreased over the first few hours to very low values (~ 0.1 $\mu A/cm^2$). The specimens pre-exposed at +600 mV SCE for two weeks showed an average increase in CPT of 8°C for SMA welds, although no increase was observed for the single GTAW weld. As this was only a single result it is not known whether GTA welds would also increase their CPT after pre-exposure.

Gartland (3) reports that this kind of pre-exposure is used in the Norwegian oil and gas industry to improve the performance of 6Mo austenitic alloys (ie. exposure in low temperature chlorinated sea water). Gartland states that this cannot be explained by film thickening because very little would occur with such highly alloyed material. It is possible that this type of exposure removes defects in the film where localised corrosion might occur at higher temperatures. The treatment certainly produced improved resistance at elevated temperatures for the super duplex stainless steel welds, but not as much as might be expected from the experiences on the platform operating at a sea water discharge temperature of 65°C (1). This may be connected with the effects of flow, in that the laboratory tests were only agitated by the air bubbling through the cell.

The potential of super duplex stainless steel in sea water varies with the chlorine concentration (5). It has been suggested that in sea water discharge lines, where the water will be warmest, the chlorine level will be lower than the normal 0.5 to 1.0 mg/l concentration. This is because it will decrease as it reacts with the biological/organic material in the sea water. Although there is no published data, it is believed that the concentration of chlorine in the discharge lines would probably be 0 to 0.3 mg/l. This would result in a potential not exceeding + 300 mV SCE (5).

A single weld was exposed for ten days in aerated sea water at room temperature. For the first 7 days the potential was not controlled and it gradually increased to about –100 mV SCE. The potential was then increased by 100 mV every 24 hours for a further 3 days. The specimen was then exposed to a normal CPT test, but at a potential of +300 mV SCE. The resultant CPT was 50°C. This was a little lower than obtained after pre-exposure at +600 mV, but may be just at the extreme of data spread. At first sight exposure at +300 mV rather than +600 mV might be expected to result in higher CPT values. However, Gartland (3) reports that over the potential range +1000 mV to +300 mV there is hardly any change in CPT for high alloy stainless steels in sea water. Only if the potential decreased to between 0 and +100 mV SCE would a significant change in CPT be found.

The samples that were passivated in nitric acid both showed an increase in CPT compared with the samples with no pre-treatment. The average increase was 13°C, which is more than that obtained by pre-exposure in sea water. It is believed that the action of nitric acid is twofold.

Because of its highly oxidising nature it tends to thicken up the passive film, and it can also remove some of the surface inhomogeneities, such as inclusions, on the surface.

The samples that were pickled showed the largest increase in CPT. The average increase was 25°C. This is a phenomenal increase in pitting resistance, and gives the welds only slightly inferior pitting resistance to the parent material (CPT~90°C). It is believed that pickling performs two functions that give the improved corrosion resistance. Firstly the pickling solution removes most of the surface inclusions. Also the solution will preferentially attack areas of lower corrosion resistance, i.e. areas of chromium and/or molybdenum depletion, and the resulting surface will be almost free of inclusions and other forms of alloy inhomogeneity. Hence the passive film which forms during the subsequent washing and air exposure will be significantly better than that on as–welded material. It is the presence of the fluoride in the pickling solution which enables the active dissolution of areas of reduced corrosion resistance.

The results clearly show that all of the methods investigated improve the CPT of super duplex stainless steel welds, but pickling clearly gave the largest increase.

FURTHER TESTS

Pre-exposure in cold, chlorinated sea water to condition the welds is clearly possible for piping systems in many applications, while passivation or pickling is not. However, for vessels, or other large fabrications, pickling could be considered for improving the corrosion resistance of welds. The laboratory procedure that was used is clearly not possible in the field, but commercial pickling pastes and gels are available for cleaning stainless steel welds at room temperature. Experience shows that those originally developed for 300 series stainless steels do not work well on duplex stainless steels, but some companies have developed special formulations for this application.

Tests were conducted using two such products, GP gel * and PN paste *. GTA welds were made in a 4mm plate as described previously and designated OC9067 and tests were conducted as before with three surface finishes:

1) As-welded and wire brushed.

2) Pickled with paste or gel for 30 minutes and washed in tap water.

3) Pickled with paste or gel for 1.5 hours and washed in tap water.

As before, all pickled welds were allowed to passivate in air for 24 hours prior to testing.

ASTM G48 Method A Results

In the previous tests the welded samples first showed pitting at 55° to 60°C. A sample of OC9567 first showed signs at 55°C. This was the same temperature as the GTA weld in the

* Trade mark of Anopol Ltd.

previous tests and shows that there was no significant difference between this plate and those examined previously.

Sea Water Results

Table 3 summaries the results of the CPT tests. The results for wire brushed welds gave a mean CPT of about 50° ± 2°C. This is about 4°C greater than in the previous tests. The reason for this increase is not known, but may just represent an extreme of weld to weld variation.

What is immediately apparent is that the results for pickled samples show an increase in CPT. A half hour exposure increased the CPT by 3° to 4°C, but a 1.5 hour exposure produced an increase of CPT of about 12°C.

There was no significant difference between the paste and the gel. Although the increase in CPT is not as great as was achieved by aqueous pickling for 2 hours @ 55°C, it is still substantial, and represents a significant increase in weld corrosion resistance.

The reason for the 1.5 hour exposure being more effective than 1 /2 hour may be because there is an incubation time before the pickling paste/gel activates the metal surface. This is not surprising for a high alloy material like super duplex stainless steel. The paste and gel are obviously more aggressive at room temperature than normal aqueous pickling solutions to produce such a marked effect.

These specialised pickling pastes and gels have usually been developed for 22 Cr duplex stainless steel (UNS S31803) and the higher alloy content of super duplex stainless steel means that it will obviously require a longer time for adequate pickling.

CONCLUSIONS

1) The typical CPT for super duplex stainless steel welds at +600 mV SCE in sea water is 48 ± 4°C.

2) The CPT can be increased by prolonged exposure at + 600 mV SCE in ambient temperature, aerated sea water, or passivating in nitric acid, or pickling in nitric/hydrofluoric acid.

3) The pickling produced the greatest increase in CPT, of ~ 24°C.

4) Pickling at room temperature with special paste or gel for 1½ hours gave an increase in CPT of 12°C compared with an as-welded and wire brushed finish.

RECOMMENDATIONS

For vessels and large fabrications, where the part of the weld that will see process fluids is accessible, then pickling with special paste or gel for 1½ hours will give a significant increase in CPT. With piping systems pickling is not practical and so a gentle start up with sea water exposure is recommended. One regime that has been used in the North Sea is:-

1) Run the sea water system untreated for a minimum of 48 hours.

2) Turn on the chlorination (0.5 to 1.0 mg/l at the inlet), without heat transfer, and run for a minimum of 5 days.

3) Start heat exchangers. Try to avoid very high (> 50°C) discharge temperatures).

The successful example quoted in the introduction operated at a discharge temperature of ~ 20°C for two to three months before increasing to 50° to 55°C for two years and then going to 65°C. This suggests that a gentle start up is very beneficial.

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TABLE 1. Results of ASTM G48A critical pitting temperature tests

Temp. (°C)	Weight Loss (mg)		
	OC8511/A	**OC8511/B**	**OC8511/C**
30	9	12	8
35	0	0	0
40	1	0	0
45	0	0	1
50	0	1	0
55	1,000	0	0
60	-	176	264

TABLE 2. Results of critical pitting temperature tests in seawater (all at 600mV SCE and 5°C/hr ramp rate)

Sample No.	Weld Type	Surface Pretreatment	CPT (°C)
A1	GTAW	None	47
A2	GTAW	None	46
B1	SMAW	None	44
B2	SMAW	None	45
A3	GTAW	2 weeks @ 600mV SCE @ 20°C	47
A4	GTAW	ditto	*
B3	SMAW	ditto	51
B4	SMAW	ditto	54
C1	SMAW	Passivated for 20 mins @ 20°C	57
C2	SMAW	Passivated for 20 mins @ 20°C	60
C3	SMAW	Pickled for 2hrs @ 55°C	65
C4	SMAW	Pickled for 2 hrs @ 55°C	60

* electrical fault during test

TABLE 3. Results of further critical pitting temperature tests in sea water (all at +600 mV SCE and 5°C/hr ramp rate)

OC No.	WELD TYPE	SURFACE PRETREATMENT	CPT (°C)
9067/A	GTA	Wire brushed	52
9067/B	GTA	Wire brushed	48
9067/D	GTA	Wire brushed	48
9067/F	GTA	Wire brushed	51
9067/G	GTA	pickled 0.5 hr PN paste	54
9067/H	GTA	pickled 0.5 hr GP gel	53
9067/C	GTA	pickled 1.5 hr PN paste	64
9067/E	GTA	pickled 1.5 hr GP gel	61

FIGURE 1 Current versus time curve for welded super duplex stainless steel in sea water at +600mV SCE

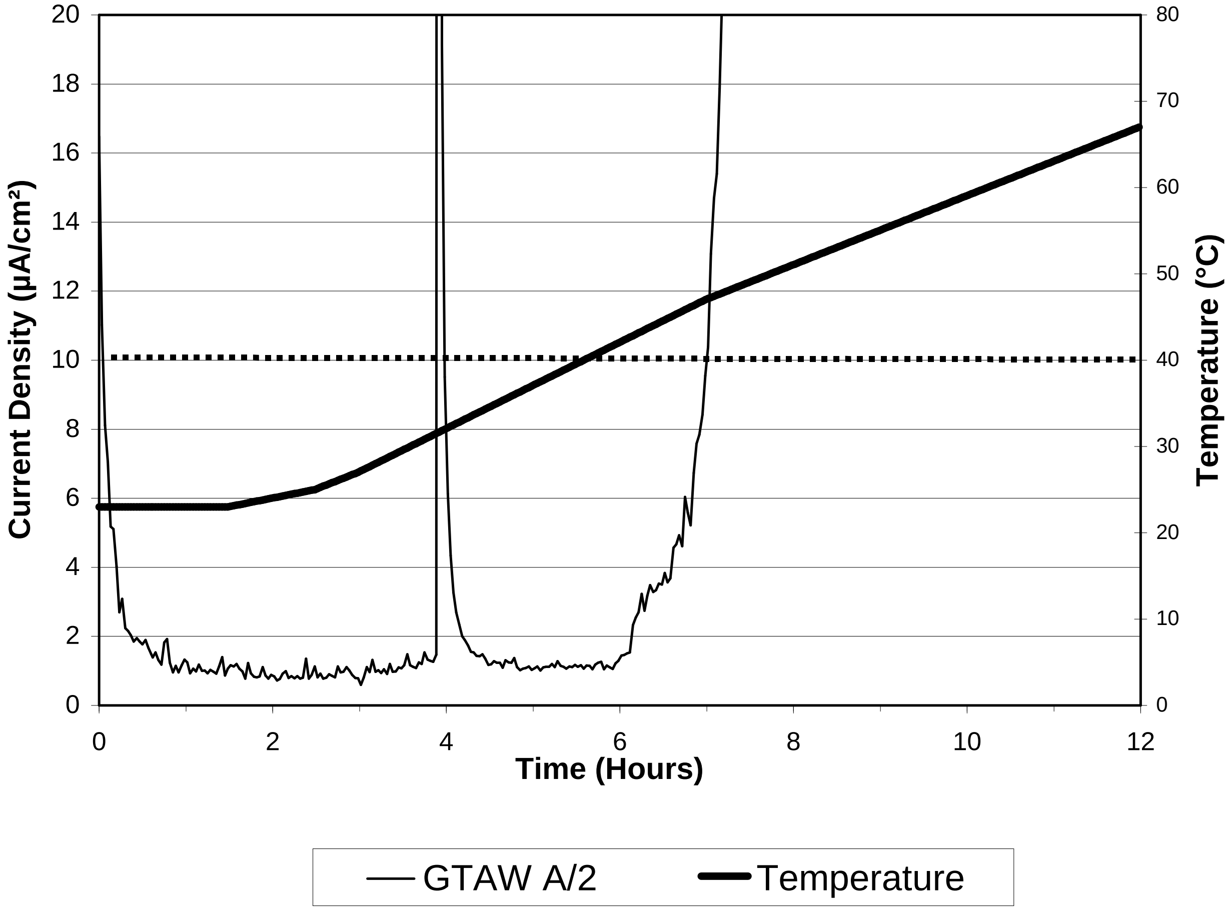

FIGURE 2 Current versus time curve for welded super duplex stainless steel in sea water at +600mV SCE

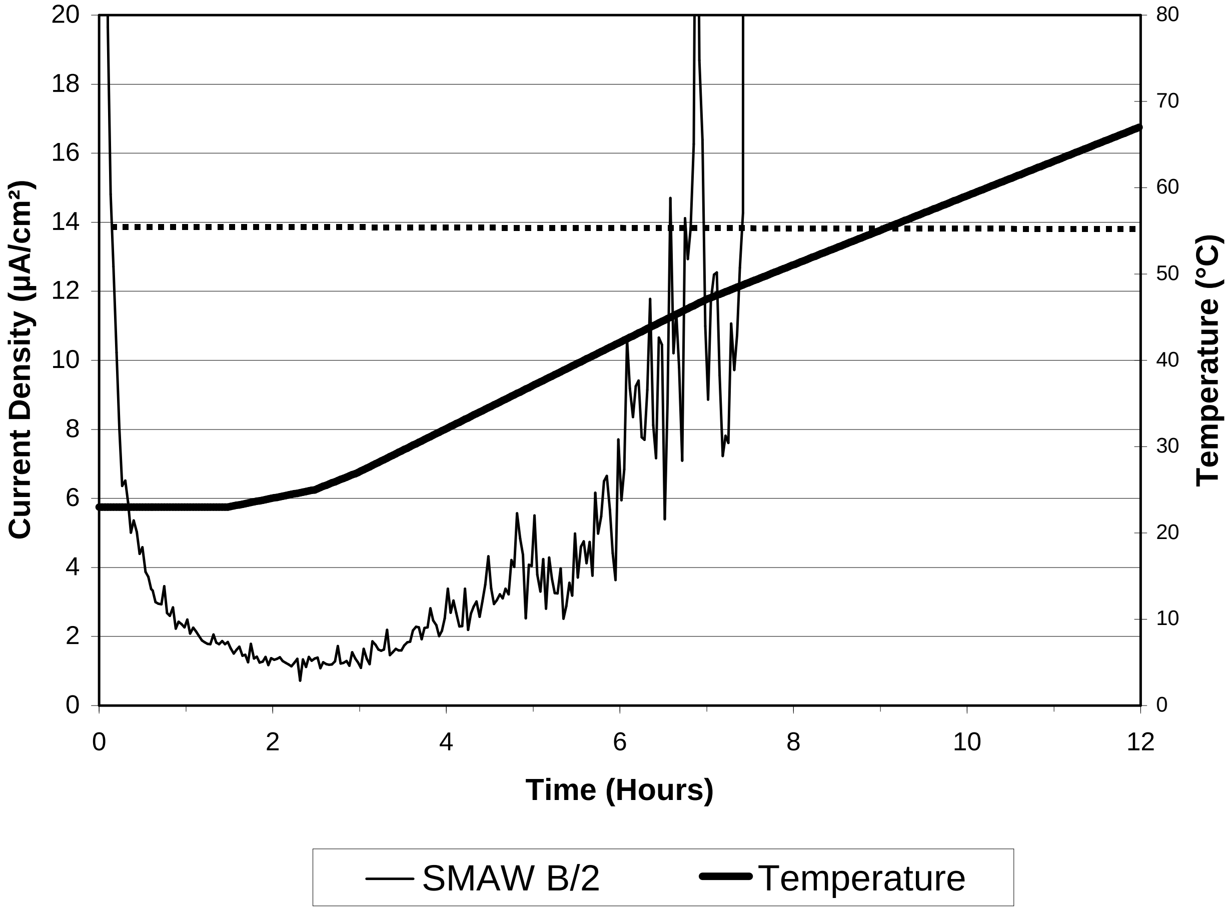

FIGURE 3 Current density versus time during exposure at 600mV SCE in sea water at room temperature