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## PITTING TEMPERATURE OF DUPLEX STAINLESS STEELS IN OILFIELD ENVIRONMENTS

<sup>1</sup>Department of Metallurgical & Materials Engineering, The Federal University of Technology, Akure, NIGERIA

**Abstract:** The critical pitting temperatures of some selected duplex stainless steels have been determined. Potentiostatic polarisation was conducted for all the alloys in aerated and CO<sub>2</sub>-saturated oilfield brine. A constant potential of 250 mV versus Ag/AgCl was applied and the temperature of the solution was ramped at 1°C/second. The critical pitting temperature was determined as the temperature at which the current densities of the alloys exceeded 100 µA/cm<sup>2</sup>. Results showed that the critical pitting temperature was lower for the alloys in the CO<sub>2</sub>-saturated oilfield brine compared with the aerated environment. Also, the pitting resistance equivalent number did not seem to determine the resistance of the lean duplex stainless steels as UNS S32101 and UNS S32304 with equivalent PREN exhibited different pitting temperatures.

**Keywords:** Pitting, oilfield brine, stainless steels, PREN

### INTRODUCTION

Duplex stainless steels are specifically designed to be used in aggressive environments where both corrosion resistance and mechanical properties of 300 series austenitic stainless steels are inadequate (Ezubar, 2010). The major limitation to the use of these alloys has been the high cost of the materials (Singh et al., 2007). The recent surge in the price of nickel and molybdenum has driven the cost of production of duplex stainless steels higher. However, the development of lean duplex stainless steels with much lower nickel and molybdenum content can offset some of the cost issues (Gudme and Nielsen; Rommerskirchen et al., 2009; Rao, saithala et al., 2011). The austenite phase in such alloys has been maintained by adding more manganese and nitrogen. With the development of lean duplex stainless steels, material cost is reduced, duplex microstructure is retained and the steel still retains reasonable quality (Berezovskaya et al., 2008). Lean duplex stainless steels are now candidates for many oil and gas applications such as flowlines, carcass of flexible pipes, umbilical tubing, heat exchangers, separation units, cable trays and transportation vehicles (Gudme and Nielsen; Rommerskirchen et al., 2009; Jordan, 2006). Lean duplex stainless steels are also structurally stable and the phases reform easily after welding as result of nitrogen addition. However, very limited corrosion data exists on the lean duplex stainless steels in both marine and CO<sub>2</sub>-saturated saline environments.

The pitting resistance equivalent number (PREN) is the factor on which the pitting behaviour of alloys are ranked. However, the pitting behaviour of passive alloys also depends on the passive film characteristics, the temperature and composition of bulk solution (Olefjord, 1980, Oldfield, 1987). Pitting resistance equivalent number is often represented by the amount of the corrosion resistant alloying elements in the substrate alloy (%Cr +3.3%Mo +16%N). Chromium, molybdenum and nitrogen are the major alloying elements that contribute to this number as shown in the formula (Bendall, 1996). However, the characteristics of the passive film on stainless steels is different from the substrate alloy. The passive film composition is however dependent on the substrate's composition and the corrosion medium (Olsson and Landolt, 2003). Alloying elements have been reported to be enriched in the passive film of passive alloys (Olsson and Landolt, 2003; Newman, 2001). Molybdenum and chromium are reported to be present in the passive film while nickel is said to be either absent or have very negligibly presence in the oxide film. However, it is said that the nickel is enriched just below the oxide film (Newman, 2001; Qiu, 2002). The pitting behaviour of stainless steels is also said (Newman, 2001; Qiu, 2002) to be dependent on the chloride ion concentration of the corrosion medium. However, despite the importance of the passive film chemistry to pitting corrosion, the pitting resistance

equivalent number has been developed based of the alloying elements in the substrate.

The present study looks at the critical pitting temperature of duplex stainless steels. These alloys have equal proportion of ferrite and austenite and so the pitting behaviour is more complex. This is so because the alloying elements are partitioned differently in the two phases. Also, the presence of high manganese and varying nickel additions in the lean duplex alloys make the pitting characteristics different from the fully austenitic and fully ferritic alloys.

**METHODOLOGY**

Potentiostatic polarization measurements were taken for the alloys in a three electrode electrochemical set up using an Ag/AgCl reference electrode and a platinum counter electrode. The oilfield brine was initially sparged with CO<sub>2</sub> for 8 hours and kept in the laboratory shelf. Before each experiment, the oilfield brine was also sparged for one hour resulting in a pH of approximately 5.0. Moreover, CO<sub>2</sub> was continuously fed into the solution throughout the duration of the experiment. A potential of 250 mVAg/AgCl was applied for all the experiments and the temperature ramped at 1°C/minute from ambient until the current density exceeded 100 µA/cm<sup>2</sup>. The same procedure was repeated for the alloys in the oilfield brine left in aerated conditions having a pH 6.5.

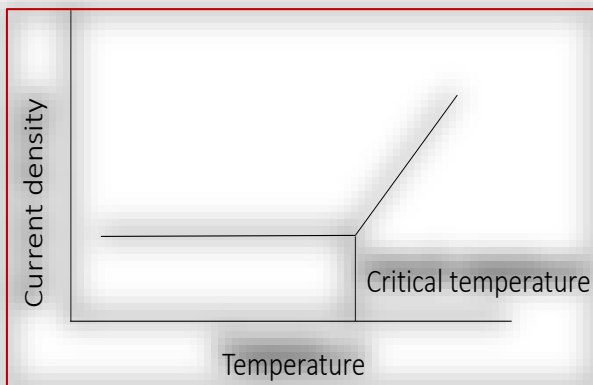


Figure 1: Schematics of how the critical pitting temperature is determined

Table 1: Properties of alloys (solution annealed conditions) used for the research

ASTM/UNS	Type	Cr	Ni	Mo	Cu	Mn	N	PREN <sub>16</sub>
S32101	Lean duplex	21.26	1.60	0.24	0.26	4.81	0.23	25.7
S32304	Lean duplex	23.00	4.80	0.30	0.25	1.00	0.10	25.5
S82441	Lean duplex	24.11	3.59	1.60	0.37	2.85	0.27	33.7
S32205	Duplex	22.43	5.73	3.15	0.24	1.40	0.18	35.7

Table 2: Oilfield brine adopted for the research

Salts	mg/L
NaCl (Sodium Chloride)	24090
KCl (Potassium Chloride)	706
CaCl <sub>2</sub> .2H <sub>2</sub> O (Calcium Chloride Di-hydrate)	1387
MgCl <sub>2</sub> (Magnesium Chloride)	4360
BaCl <sub>2</sub> .2H <sub>2</sub> O (Barium Chloride Di-hydrate)	16
SrCl <sub>2</sub> .6H <sub>2</sub> O (Strontium Chloride Hexa-hydrate)	33
Na <sub>2</sub> SO <sub>4</sub> (Sodium Sulphate)	3522
NaHCO <sub>3</sub> (Sodium Bicarbonate)	304

**RESULTS**

Figures 2, 3 and 4 show the critical pitting temperature of the alloys. The results obtained show that the critical pitting temperature is lower in CO<sub>2</sub> saturated oilfield brine than the aerated environment for all the alloys. Lean duplex UNS S32101 has pitting temperature of 23 °C and 25 °C in CO<sub>2</sub> saturated oilfield brine and aerated environments respectively. UNS S32304 has pitting temperature of 30°C and 33°C in CO<sub>2</sub> saturated oilfield brine and aerated environments respectively. UNS S28441 has very close values of 37 and 38°C in CO<sub>2</sub> and aerated environments respectively. UNS S32205 has critical pitting temperature of 50 and 58°C in CO<sub>2</sub> and aerated environments respectively.

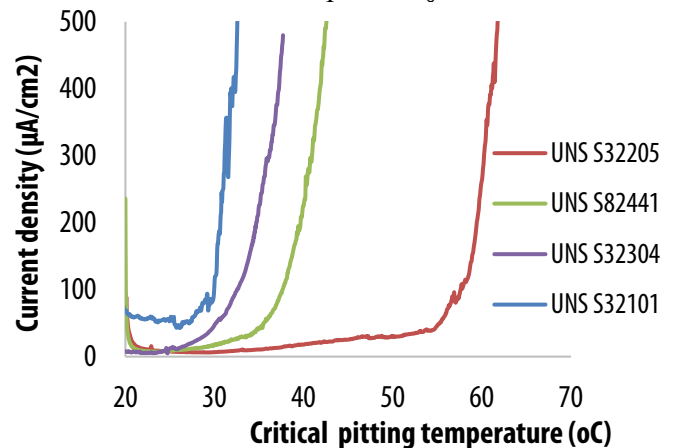


Figure 2: Critical pitting temperature in aerated oilfield environment

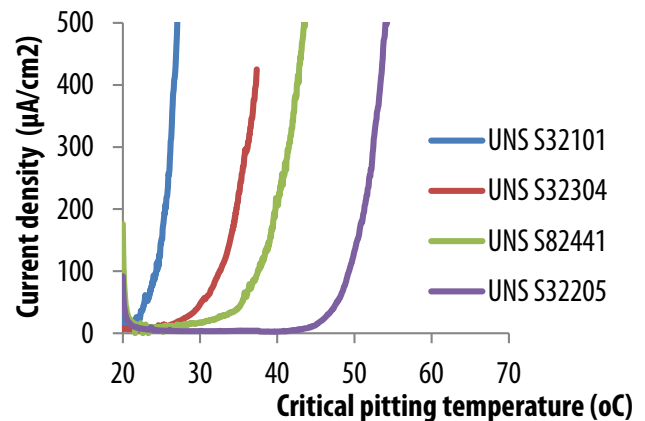
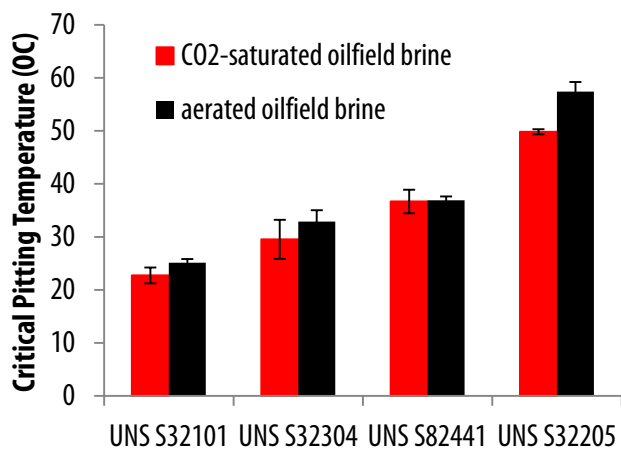


Figure 3. Critical pitting temperature in CO<sub>2</sub> saturated oilfield environment



**Figure 4.** Critical pitting temperatures of the alloys in both aerated and CO<sub>2</sub>-saturated oilfield environments

### DISCUSSION

The critical pitting temperature is lower in CO<sub>2</sub> saturated oilfield brine than aerated brine for all the alloys. Standard duplex UNS S32205 and UNS S82441 seem to exhibit differences in their pitting characteristics. Both alloys however, exhibit higher pitting temperature expected of highly alloy steels. However, UNS S32205 exhibited higher pitting temperature than UNS S82441. Another observation is that the lean duplex UNS S32304 has a higher pitting temperature compared to UNS S32101 in both environments.

Acidification resulting from the dissolution of CO<sub>2</sub> in water to form carbonic acid is thought to be a reason for the aggressiveness of the CO<sub>2</sub> saturated oilfield compared with the aerated environment. Also, lower oxygen content of CO<sub>2</sub> saturated environment would render the passive structurally defective and less dense (Anselmo *et al.*, 2006).

Possibility of chloride ion adsorption and incorporation in the passive film formed on passive alloys has also been reported (Olsson and Landolt, 2003; Hubschmid *et al.*, 1995; Landolt *et al.*, 1990; Virtanen *et al.*, 1994). According to Anselmo *et al.*, 2006, the behaviour of passive film in CO<sub>2</sub> saturated environment is dependent on the synergistic effects of both chloride ion concentration and CO<sub>2</sub>. According to these authors, at higher chloride ion concentration (40,000-80,000ppm) the pitting potentials of martensitic stainless steel is lower in CO<sub>2</sub> saturated environment as compared to aerated seawater environment. They also argued that the pitting behaviour changed at lower chloride concentration (20,000-30,000 ppm).

Both the chemistry of the near surface of the bulk alloy and that of the passive film are important to the resistance of alloys to pit formation (Elsener *et al.*, 2011a, Elsener *et al.*, 2011b). Elsener *et al.*, 2011a) reported nickel enrichment at the interface between the bulk and the passive film formed on UNS S30400 and UNS S31803 after exposure to an alkaline

medium for 24 hours. UNS S32304 and UNS S32101 have similar pitting resistance equivalent number (PREN) as shown in Table 1. However the two alloys exhibited differences in their pitting characteristics. This is thought to be as a result of the differences in the chromium and nickel additions as well as the higher manganese in UNS S32101.

Higher nickel content of the bulk UNS S32304 may result in a higher enrichment of nickel (Olefjord, 1980, Elsener *et al.*, 2011; Lorang *et al.*, 1994) at the interface between the bulk alloy and the passive film. This is in addition to the higher chromium expected in the passive film of UNS S32304. The lean duplex alloy UNS S32101 on the other hand has higher manganese and lower nickel addition in the bulk. This could make the layer below the passive film have less nickel enrichment and the passive film of high manganese addition. Manganese being an active (Elsener *et al.*, 2011a; Elsener *et al.*, 2011b) element is then dissolved into the solution leaving the passive film defective. There is therefore a need to incorporate the factors of nickel and manganese into the pitting resistance equivalent number for the lean duplex stainless steels.

Addition of 3.15 wt. % molybdenum in UNS S32205 seems to outweigh the higher chromium addition in UNS S82441. Hence, the higher pitting temperature attained by UNS S32205.

### CONCLUSIONS

The critical pitting temperatures of some selected duplex stainless steels have been determined. Potentiostatic polarisation was conducted for all the alloys in aerated and CO<sub>2</sub>-saturated oilfield brine. A constant potential of 250 mV versus Ag/AgCl was applied and the temperature of the solution was ramped at 1°C/second. The critical pitting temperature was determined as the temperature at which the current densities of the alloys exceeded 100 µA/cm<sup>2</sup>. Results showed that the critical pitting temperature was lower for the alloys in the CO<sub>2</sub>-saturated oilfield brine compared with the aerated environment. Also, the pitting resistance equivalent number did not seem to determine the resistance of the lean duplex stainless steels as UNS S32101 and UNS S32304 with equivalent PREN exhibited different pitting temperatures.

1. Critical pitting temperature is lower for the alloys in the CO<sub>2</sub>-saturated oilfield brine compared with the aerated environment.
2. The pitting resistance equivalent number does not seem to determine the resistance of the lean duplex stainless steels as UNS S32101 and UNS S32304 with equivalent PREN exhibit different pitting temperatures.
3. UNS S32205 has a higher pitting resistance compared with UNS S82441 in both environments

4. UNS S32304 has a higher pitting resistance compared with UNS S32101 in both environments
5. There seems to be a wide margin between the pitting temperature of UNS S82441 and UNS S32205

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