



## CORROSION BEHAVIOUR OF 25Cr SUPER DUPLEX IN HIGH SULPHATE ENVIRONMENT

A. Ismail

Department of Materials and Design Engineering, Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Malaysia

E-Mail: [azzura@uthm.edu.my](mailto:azzura@uthm.edu.my)

### ABSTRACT

Super super duplex stainless steel has shown excellent performance against corrosion attack. However, in corrosive media, 25Cr super duplex is susceptible to localised corrosion attack, especially in seawater and high temperatures. Therefore, the application of this high price material becomes useless when corrosion is likely to attack. The corrosiveness of media increases as the anion content increases. This paper presents the corrosion mechanism of 25Cr super duplex exposed to a high concentration of sulphate in the salinity of seawater. The solution (media) was prepared according to the same composition as seawater including pH, salinity and dissolved oxygen. The corrosion mechanism was characterized as breakdown potential ( $E_b$ ) (also known as the pitting potential) of 25Cr super duplex, which is, the potential once reaches a sufficiently positive value. The  $E_b$  values of 25Cr super duplex were identified at 4 °C, 20 °C, 50 °C and 80 °C, and the  $E_b$  values in high sulphate content and in seawater were compared for the same temperature range. The results showed that the  $E_b$  values decreased in all solutions at increased temperatures due to the increasing attack of localized corrosion. The corrosion attack become worse as the sulphate content in seawater increase cause the decreasing the  $E_b$  value, which indicated that the sulphate anions accelerated the corrosion attack on 25Cr super duplex. The conclusion is, although some researchers claim that sulphate ion inhibite corrosion attack on corrosion resistant alloys (CRAs), but for super duplex alloy, the sulphate ion accelerate localised corrosion attack.

**Keywords:** seawater, breakdown potential, anion, open circuit potential, localized corrosion.

### INTRODUCTION

25Cr super duplex has been widely used in industrial components for decades due to its well-documented resistance to corrosion, high strength with moderate alloy cost (lower Ni and Mo content). 25Cr super duplex have a complex microstructure with comparable volume of austenite and ferrite. The highly mobile ions move around and form an outer region of the passive film that is independent of the underlying phase (having either an austenitic or a ferritic structure) and enhances the protective properties of the passive film. Due to differences in chemical composition between austenite and ferrite, a heterogeneous passive film may be formed on both phases. The interaction between nitrogen and molybdenum takes place in the near passive layer region becomes particular importance for the corrosion resistance of 25Cr super duplex. However, it still suffers from corrosion attack, especially in a corrosive media such as seawater. The corrosion of 25Cr super duplex in seawater is mainly dependent on the salt content (which increases the electrical conductivity) and its oxygen content. In addition, several variables can influence and complicate the course of corrosion in different ways, such as chloride, sulphate and temperature.

The CRAs, such as 25Cr super duplex, depends on the formation of naturally occurring transparent oxide films, which have a valuable effect by conferring corrosion resistance on bare metal surfaces even in aggressive environments. These films may be impaired by surface contamination, such as organic compounds or metallic or inorganic materials (Malik *et al.*, 2009). The formation of these films is by chromium oxide layer and is

assumed to be responsible for the effectiveness of the passivation. Passivity can be defined as the loss of chemical reactivity under certain conditions (Fontana, 1985). Steel achieves this by having a passive film form over its surface. The passive film is formed by the reaction of chromium with oxygen to produce chromium oxide as a protection from the surroundings. Therefore, the characterisation of stainless steel is according to the minimum 10.5% wt% Cr (Chromium) addition to iron (Roberg, 2008). This puts the steel in a passive state, and, when the film is breached, it immediately heals when oxygen is present. In electrochemical analysis, the breach of the passive film is known as the breakdown potential,  $E_b$ .

This paper reveals the corrosion performance of a 25Cr super duplex, in a high sulphate composition of seawater. Generally, the anions in seawater (such as sulphate) increased the corrosion attack on the metal surface. However, some research reveals that sulphate ions could decrease the corrosion attack by providing a protective layer on the metal surface (Haleem *et al.*, 2012). The protection surface (passive layer) occurs when sulphate were exist as a ratio with chloride. Because of obvious sizes, the competition effects occurs and therefore, sulphate becomes as a layer to protect the metal from further attack by chloride ion (Jin Li, 2013).

### THEORY AND CALCULATION

Corrosion is defined as the deterioration of a material through a chemical or electrochemical reaction with its environment (Haleem *et al.*, 2012). Materials often have a natural tendency to combine with other chemical



elements to return to their lowest energy state. Frequently, the combinations are with oxygen and water, which both are present in most natural environments, to form hydrated oxides. In the case of iron, the iron oxide is referred to as “rust”.

## EXPERIMENTAL

The corrosion mechanism was characterized to break down the potential ( $E_b$ ) of 25Cr super duplex, which is the potential once it reaches a sufficiently positive value, also known as the pitting potential.  $E_b$  is also known as the surface potential at which the passive film on the surface breaks down. This leads to an active electrochemical reaction, which causes corrosion or repassivation of the surface in certain conditions. This is the point of localized corrosion for evaluating and considering the potential, which could be an appropriate point according to any given combination of material/ambient/testing methods. The  $E_b$  values of 25Cr super duplex were identified at 4 °C, 20 °C, 50 °C and 80 °C, and the  $E_b$  values in high sulphate content and in seawater were compared for the same temperature range.

Each anodic polarisation scan was reversed once the current reached a set current ( $i_{rev}$ ) of 500  $\mu\text{A}/\text{cm}^2$ . The scan rate was set at 0.25mV/sec in static condition. The degree of increase in the current beyond  $i_{rev}$  gives an indication of the propensity for the propagation of corrosion (Thomson and Payer, 2012). An indication of the extent of propagation is therefore obtained by consideration of  $i_{max}$ , which represents the maximum current attained should the current not begin to fall immediately after scan reversal.

## RESULTS AND DISCUSSION

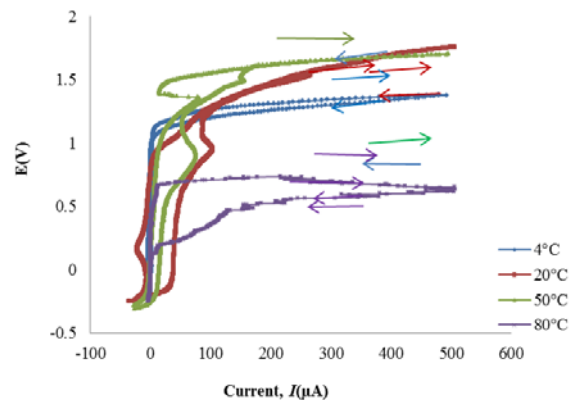
In anodic polarisation tests, the electrode potential of the material is scanned from the free corrosion potential ( $E_{corr}$ ), also known as the Open Circuit Potential (OCP), in the more positive direction at a fixed rate. When passivity is exhibited, the current initially remains very small. Once the potential reaches the breakdown potential ( $E_b$ ) (at which the passive film breaks down due to the overpotential driving force), the current suddenly increases. The breakdown potential of the material provides information concerning the resistance of materials to passivity breakdown (T. Laitinen, 2012).

This experiment was conducted to quantify the effect of sulphate (Table-1) on the corrosion attack of 25Cr super duplex. For passive alloys, corrosion resistance is provided by a very thin invisible film of oxide on the surface, known as a passive film, which is formed by the metal reacting with the ambient environment. Although normally these films are free of pores, their stability may be weakened locally in an environment containing aggressive anions. The composition of seawater was maintained in the same salinity (worldwide seawater salinity is 3.5%) for both solutions to avoid the effect of other ions on the corrosion attack.

**Table-1.** Composition of seawater and high sulphate seawater.

Component	Seawater (g/kg)	High sulphate seawater (g/kg)
Chloride ( $\text{Cl}^-$ )	19.25	1.09
Sulphate ( $\text{SO}_4^{2-}$ )	2.71	20.87
Magnesium	1.30	1.30
Calcium ( $\text{Ca}^{2+}$ )	0.42	0.42
Potassium ( $\text{K}^+$ )	0.39	0.39
Sodium ( $\text{Na}^+$ )	10.71	10.71
<b>Concentration</b>	<b>34.78</b>	<b>34.78</b>

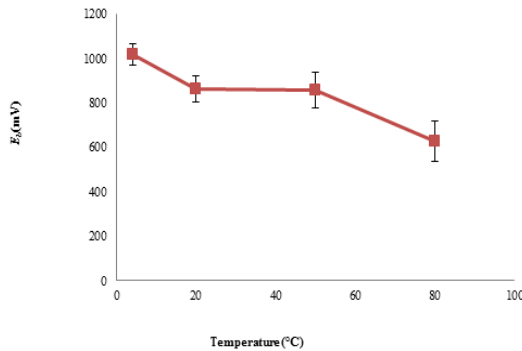
Figure-1 shows 25Cr super duplex in a solution with a higher sulphate content compared to seawater (same salinity) at 4 °C, 20 °C, 50 °C and 80 °C. The cyclic polarisation performs in positive hysteresis at all temperatures, which indicates that after the passive film is destroyed, the material does not repair itself. Therefore, the corrosion attack is propagated and localised corrosion will start.



**Figure-1.** The cyclic polarisation of 25Cr super duplex in high sulphate seawater at different temperatures.

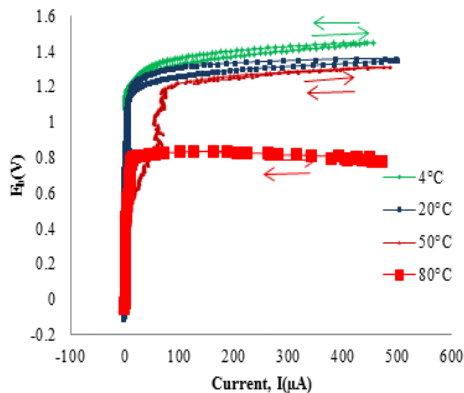
The presence of a high sulphate content causes the distribution of the available pit sites to shift to a higher potential, which causes pit propagation in both metastable and stable states (Laitinen, 2000).

Figure-2 presents the breakdown potential,  $E_b$ , as a function of temperature. The  $E_b$  value decreases as the temperature increases, which indicates that the corrosion resistance of 25Cr super duplex decreases as the temperature increases. The material corrodes easily as the temperature increases due to the high mobility of aggressive anions (A. Ismail, 2014; Vasyliov, 2015; Digby *et al.*, 2015). The mobility effect was obeyed the Arrhenius equation.



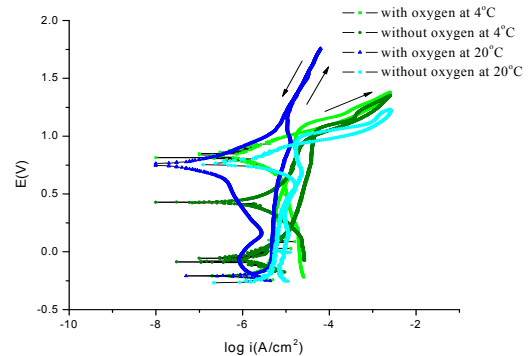
**Figure-2.** The breakdown potential at increasing temperature in high sulphate seawater.

Figure-3 presents the cyclic polarisation of 25Cr super duplex in seawater. This is to compare the performance of 25Cr super duplex in seawater and seawater with high sulphate content. Similar to 25Cr super duplex in seawater with high sulphate content, the polarisation presents as positive hysteresis at temperatures of 4 °C, 20 °C, 50 °C and 80 °C. There is a significant reduction in  $E_b$  as the temperature increases, which explains the reduction in the corrosion resistance of the material to corrosion attack.



**Figure-3.** The cyclic polarisation of 25Cr super duplex in seawater at different temperatures.

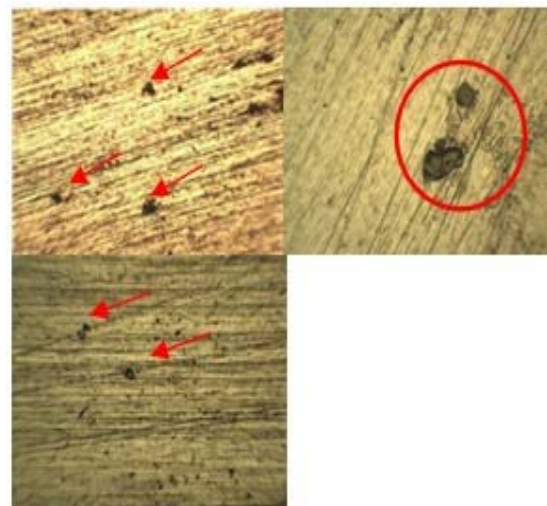
The positive hysteresis could indicate that the passive film damage is not repaired and allows pits to initiate (Tait, 1994). However, the  $E_b$  value is higher than the  $E_b$  value for the high sulphate content for all temperatures, which reveals that 25Cr super duplex is more susceptible to localised attack in high sulphate seawater (Figure-4).



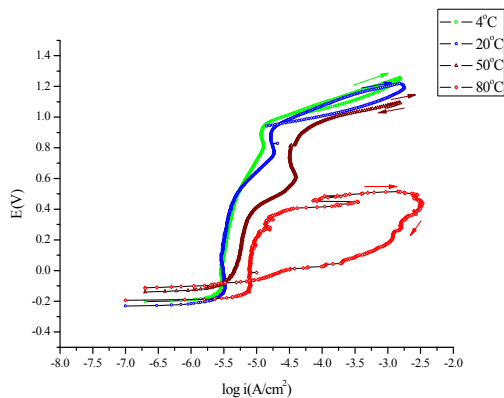
**Figure-4.** The breakdown potential at increasing temperature in seawater.

Figure-5 presents the optical view of some pits that developed on 25Cr super duplex at 80 °C in high sulphate seawater. However, the pits are shallow and the coupons are still clean from the pits if observed with the naked eye.

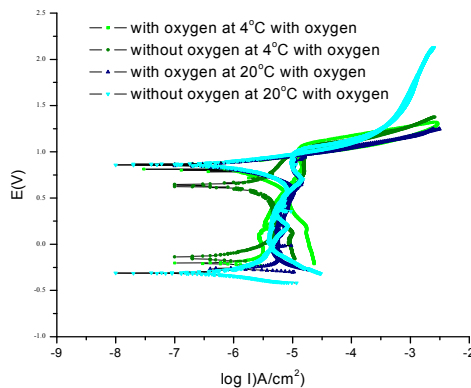
The experiment was continued by observing the effect of the  $E_b$  values in respect of the effect of oxygen (Figure-6 and 7). Figure-8 indicates that with no oxygen concentration in the seawater, the  $E_b$  values increase, and the values show the same trends, as the  $E_b$  values are higher in seawater compared to those for high sulphate seawater. The results reveal that the corrosion attack on 25Cr super duplex can be controlled or minimised in deaerated solutions. However, in other passive alloys, such as SS316L, sulphate creates competition between the sulphate and chloride to form another protective layer on the metal surface (W.S. Tait, 1994).



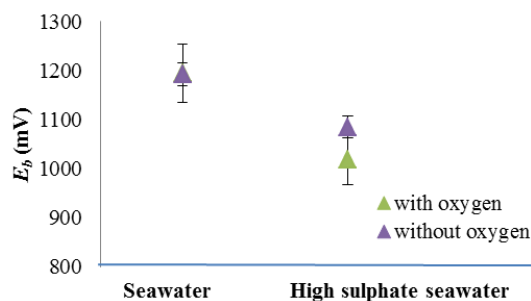
**Figure-5.** Some pitting observed at high temperatures in seawater.



**Figure-6.** The cyclic polarisation of 25Cr super duplex in high sulphate seawater with deaerated oxygen.



**Figure-7.** The cyclic polarisation of 25Cr super duplex in seawater with deaerated oxygen.



**Figure-8.** The cyclic polarisation of 25Cr super duplex in seawater with no oxygen.

## CONCLUSIONS

The corrosion resistance of the material reduced as the temperature increased. The 25Cr super duplex shows higher breakdown potential in seawater compared to high sulphate seawater. The same trend was observed in deaerated seawater, which explains that the corrosion resistance of materials to corrosion attack increases when there is no oxygen in the seawater even though, oxygen is

important for building a passive film (chromium oxide). The sulphate ions increased the corrosion attack on 25Cr super duplex.

## ACKNOWLEDGEMENTS

The author would like to acknowledge the Ministry of Education Malaysia and Universiti Tun Hussein Onn Malaysia for funding this research under the research of FRGS 2014/1 Vot number 1460.

## REFERENCES

- [1] A.Ismail, Corrosion Behavior Of Austenitic Stainless Steel In High Sulphate Content, (2014), Advanced Materials Research. Vol. 893. pp 397-401.
- [2] A.Ismail, (2014), Corrosion Behavior of WC-Co In High Sulphate Content, Advanced Materials Research, Vol. 911. pp 82-86.
- [3] A.U. Malik, M. Kutty, N.A. Siddiqi, I.N. Andijani, & S. Ahmad, (2009). Corrosion Studies on SS 316 L in Low pH High Chloride Product. Corrosion Science, pp 76-81.
- [4] Digby, D.M., Samin S., Feixiong. M., Pin. Lu., Bruno. K., (2015). Exploration of the effect of chloride ion concentration and temperature on pitting corrosion of carbon steel in saturated  $\text{Ca(OH)}_2$  solution. Corrosion Science, 98, pp.708-715.
- [5] El-Naggar M.M.(2001), Effects of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  anions on the anodic behavior of carbon steel in deaerated 0.50 M  $\text{NaHCO}_3$  solutions, Applied Surface Science, . 252(18).
- [6] M.G. Fontana. (1985), Corrosion Engineering, McGraw-Hill, pp. 3-13.
- [7] N.G Thompson & J.H. Payer, DC electrochemical test methods. Vol. 6. pp 98.
- [8] P.L. Manganon, (1999), The Principles of Materials Selection for Engineering Design, Prentice Hall, pp.512-535.
- [9] P.C. Pistorius & G.T. Burstein. (1992), Growth of corrosion pits on stainless steel in chloride solution containing dilute sulphate. Corrosion science,. 33(12): p. 1885-1897.
- [10] Roberg P.R. (2008), Corrosion engineering: Principles and practice: McGraw-Hill, pp 5, 169-177.
- [11] S.M. Abd El Haleem, S. Abd El Wanees, E.E. Abd El Aal, A. Diab, (2012), Environmental factors affecting the corrosion behavior of reinforcing steel II. Role of some anions in the initiation and inhibition of pitting



corrosion of steel in  $\text{Ca}(\text{OH})_2$  solutions, Corrosion Science, 52(2).pp 292-302.

- [12] T. Laitinen., (2000), Localized corrosion of stainless steel in chloride, sulfate and thiosulfate containing environments. Corrosion Science, 42(3): p. 421-441.
- [13] W.S. Tait, An introduction to electrochemistry corrosion testing for practicing engineers and scientist, 1994, PairODocs Publications. p. 119.
- [14] Vasyliov, G.S. (2015). The influence of flow rate on corrosion of mild steel in hot tap water. Corrosion Science, 98, pp.33-39.
- [15] V.Cicek, & B. Al-Numan, (2011), "Corrosion Chemistry", Canada: Scrivener Publishing LLC, pp 18, 19, 28.