Passivity and Corrosion of Supermartensitic Stainless Steels

Abdulaziz Moshaweh and Tim Burstein

Introduction

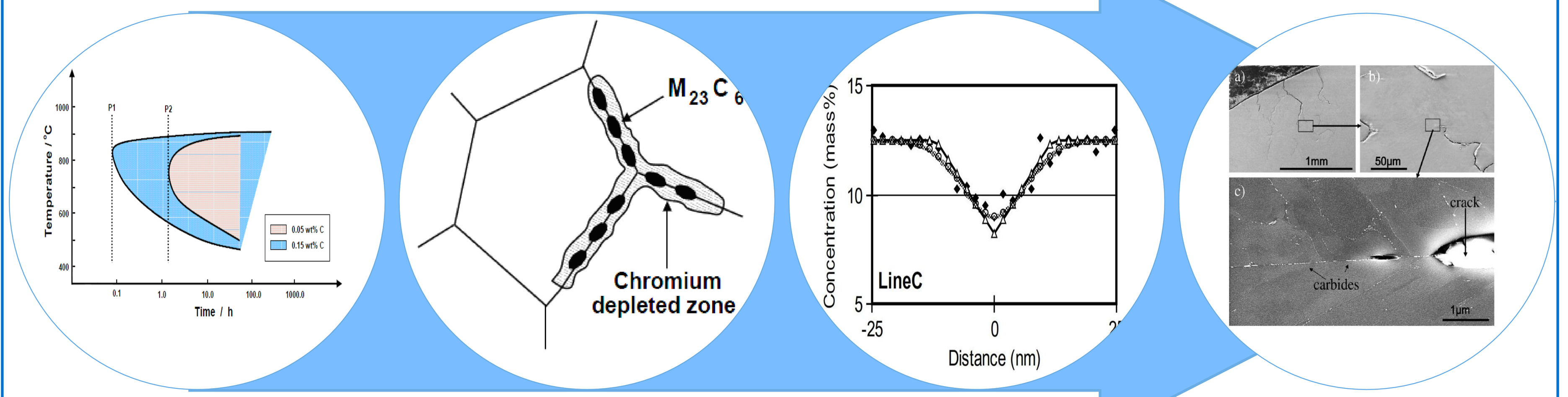
Supermartensitic stainless steels (SMSS) were recently developed to replace the more expensive stainless steels being used in the oil and gas industry. They are mainly used in down-hole application in the oil fields. They have many advantages that makes them an attractive option in the industry:

- ❑ much less expensive than other stainless steel options (3 to 5 times less)
- ❑ contains very low carbon content (<0.01 wt%)

However recent failures in the field, especially in welded sections, limit their use.

Objective

We are looking at the cause of failures of these steels, which is believed to be intergranular corrosion. Intergranular corrosion in welded parts is mainly attributed to chromium-carbide formation in the grain boundaries. This will cause chromium depleted-zones around grain boundaries that will make them vulnerable to pitting corrosion. Therefore, solving pitting corrosion problem will help in solving the problem of intergranular corrosion of these steels.



Ref. [1] Ref. [2] Ref. [3] Ref. [3]

Methods

Cyclic voltammetry (6 cycles for each condition) was used to study the pitting behaviour of SMSS. Effects of pH, chloride concentration, temperature, potential scan rates and presence of sulphates on pitting behaviour were tested.

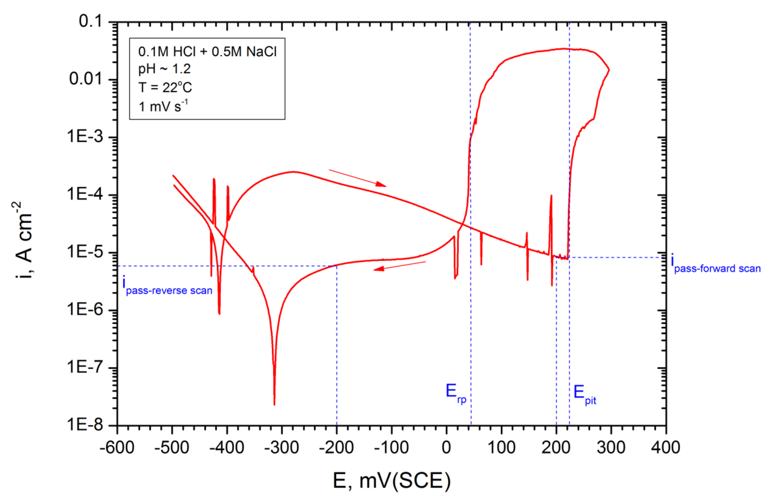
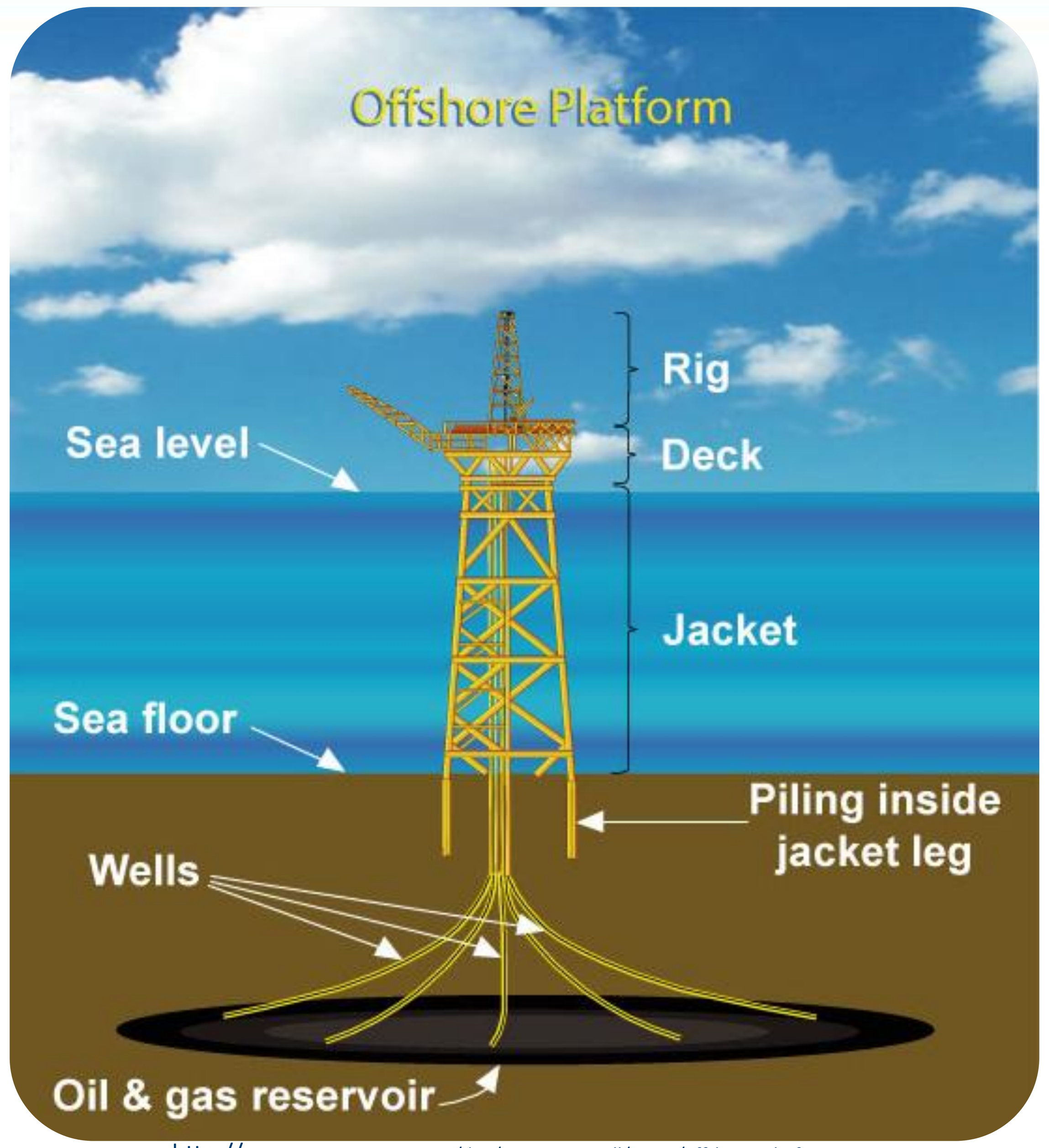


Figure 1: Cyclic voltammogram



http://www.conservation.ca.gov/dog/picture_a_well/Pages/offshore_platform.aspx

Results

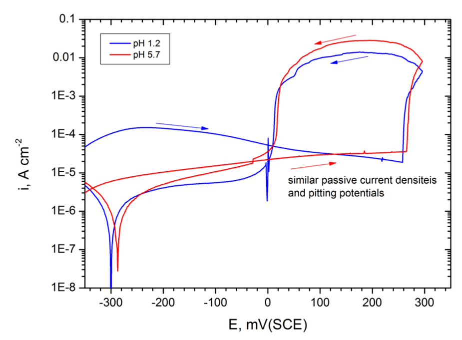


Figure 2: Effect of pH on the pitting behaviour of SMSS using 0.1M HCl + 0.5M NaCl (pH ~ 1.2) and 0.6M NaCl (pH ~ 5.7)

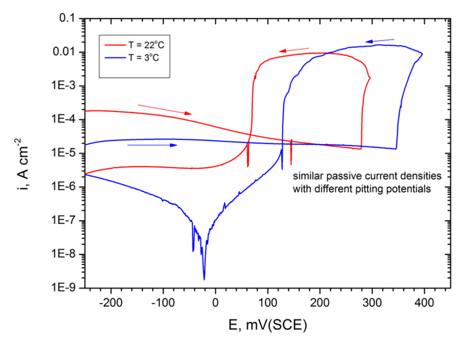


Figure 3: Effect of temperature on the pitting behaviour of SMSS at 3°C and 22°C

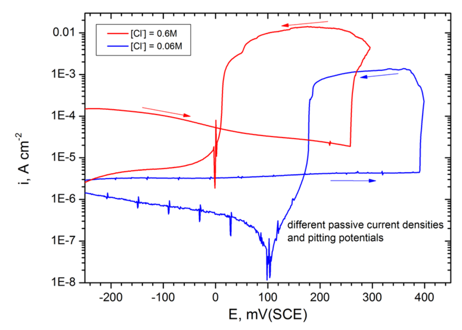


Figure 4: Effect of [Cl⁻] on the pitting behaviour of SMSS using 0.1M HCl + 0.5M NaCl and 0.01M HCl + 0.05M NaCl

Results

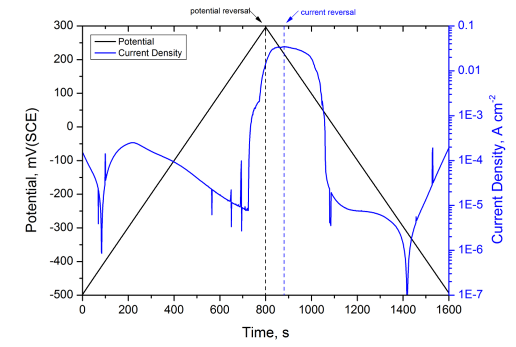


Figure 5: E and i change with time
i does not follow E after scan reversal

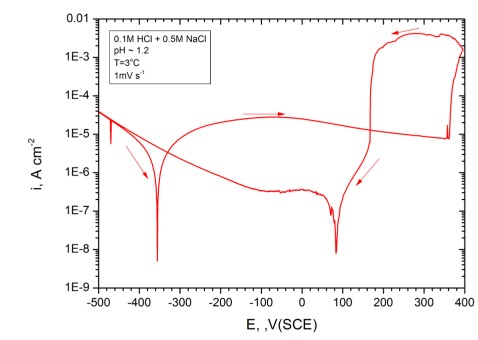


Figure 6: No i_{pass} in the reverse scan at 3°C

Discussion and Conclusions

- ❑ Although SMSS is one of the “least” alloyed stainless steels, it has E_{pit} (260 mV(SCE)) more than the higher alloyed ones (100 mV(SCE) for 304 and 150 mV(SCE) for 316L) [4].
- ❑ Carbon content plays a major role in pitting of stainless steels
- ❑ Pitting and repassivation are strongly affected by chloride concentration (-88 mV/decade) and temperature (4.44 mV K^{-1})
- ❑ Potential sweep rates as low as 1 mV s^{-1} are far from achieving steady state passivity (Figure 1).
- ❑ pH has no significant effect on pitting behaviour. [Cl⁻] affects both E_{pit} and i_{pass}.
- ❑ Pitting is a diffusion-controlled process (Figure 5) and it is independent of passive film condition (Figure 6). The main factor is the metastable-to-stable pitting transition.

Future Work

- ❑ Steady state passivity of SMSS will be studied
- ❑ Extensive surface analysis using advanced microscopy (such as EBSD, BSE SEM and TEM) will be used to identify the exact places where the pits initiate.
- ❑ Thermammetry [5] technique will be used to study the response and the effect of temperatures on SMSS.
- ❑ Electrochemical noise will be used to study metastable pitting behaviour.
- ❑ Effect of hydrogen ingress on the integrity of SMSS will be investigated.
- ❑ As these steels are used in oil and gas industry, CO_2 and H_2S effects would be studied as well.

References

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[4] A U Malik, I N Andijani, and N A Siddiqi. Corrosion behavior of some conventional and high alloy stainless steels in gulf seawater. Technical report, Saline Water Conversion Corporation, KSA, 1992.
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