Corrosion Resistance of super duplex stainless steels – the influence of copper and tungsten addition on the passivity and pitting corrosion resistance

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Thursday 28th November 2019

Langley Alloys

80 YEARS OF UNIQUE METALS

1938 - 2018

Introduction

i. Super Duplex Stainless Steels (SDSS) have provided excellent service for > 50 years

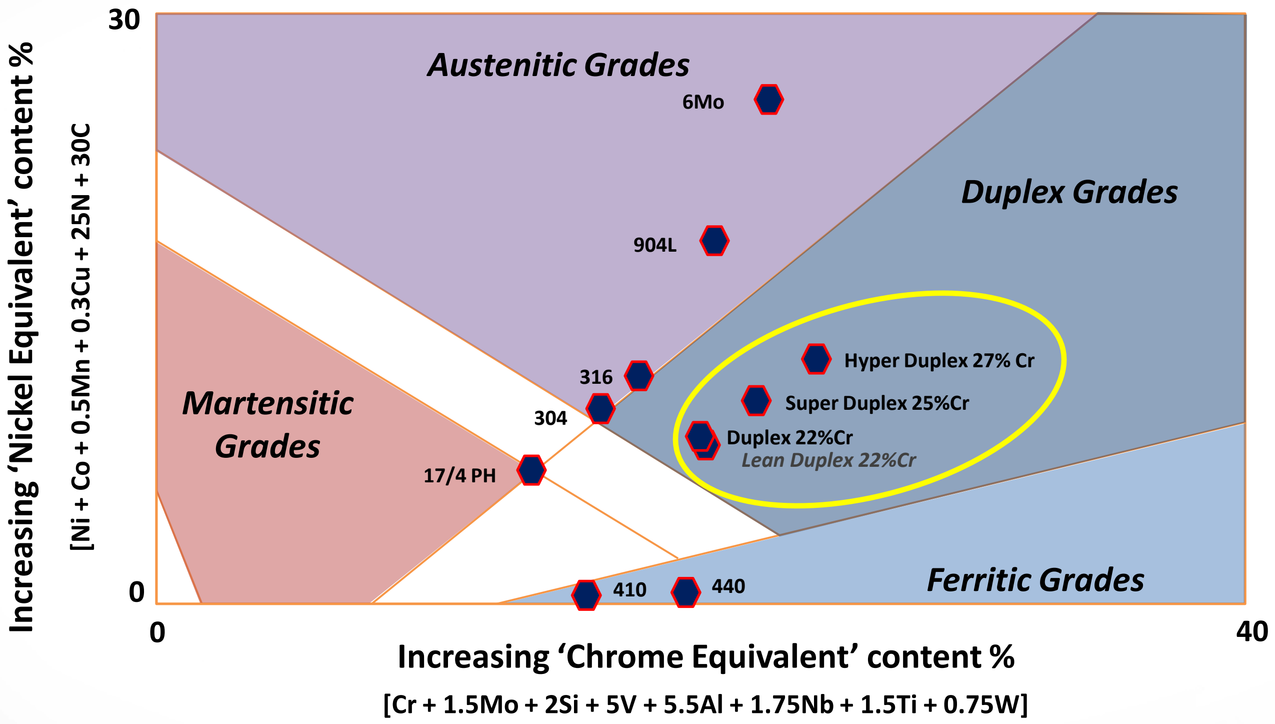
ii. Ferralium® 255 was the first commercially-available SDSS

iii. Several different SDSS alloys have subsequently been developed

iv. There are subtle differences in composition, namely Cu and W additions

v. What is our understanding of how and why these additions help ?

Super Duplex Stainless Steels (SDSS)



‘Ferralium 255’ patent application, Langley Alloys, 1967

1,158,614

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,158,614

Inventors: WILLIAM HENRY RICHARDSON and PRODYOT GUHA

Date of filing Complete Specification (under Section 3(3) of the Patents Act 1949): 14 March, 1968.

Application Date: 16 March, 1967. No. 12429/67.

Application Date: 17 March, 1967. No. 12708/67.

Complete Specification Published: 16 July, 1969.

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59/22

COMPLETE SPECIFICATION

Improvement in Stainless Steels

It has now been shown that the poor corrosion resistance of this 25% Chromium, 5% Nickel alloy, can be vastly improved by the addition of Molybdenum and Copper as shown in the following Examples *a* and *b*

Cu content is specifically mentioned with respect to corrosion resistance

However, the main claims of the patent actually relate to deliberate nitrogen additions (optimising mechanical properties + corrosion resistance).

‘Zeron 100’ patent application, Mather & Platt, 1984

(12) UK Patent Application (19) GB (11) 2 128 632 A

(71) Applicant
Mather & Platt Limited,
(United Kingdom),
Park Works,
Manchester,
M10 6BA

(72) Inventor
Kevan John Gradwell

The addition of copper will have a beneficial effect on corrosion resistance. Thus, for example, the alloy may include copper in an amount up to 1% by weight. If greater than 0.5% by weight of copper is added, the active dissolution rate of a duplex alloy in boiling hydrochloric acid and the crevice corrosion loss in a chloride solution is also decreased.

Tungsten up to 1% by weight increases the immunity potential to crevice corrosion of a duplex alloy in high temperature chloride solutions above which crevice corrosive starts.

Cu & W content are specifically mentioned with respect to corrosion resistance.

However, much of the patent content relates to Mn content to facilitate increased nitrogen additions.

Super Duplex Stainless Steels - summary

	Ferralium® 255 (S32550)	Zeron® 100 (S32760)	SAF2507® (S32750)
Nearest UNS	S32550	S32760	S32750
Nearest DIN	1.4507	1.4501	1.4410
Trademarked - when	1969	1980	1988
Trademarked - by	**Langley Alloys**	Weir Materials → Rolled Alloys	Sandvik

Cr	24.50 – 26.50	24.00 – 26.00	24.00 – 26.00
Ni	5.50 – 6.50	6.00 – 8.00	6.00 – 8.00
Mo	3.10 – 3.80	3.00 – 5.00	3.00 – 4.00
Cu	1.50 – 2.00	0.50 – 1.00	< 0.50
W	\	0.50 – 1.00	\
P_{max}	0.025	0.035	0.030
S_{max}	0.005	0.020	0.010

Pitting Resistance Equivalent Number (PREN)

Several variations of the PREN formula have been developed.

All were developed to reflect the pitting resistance of stainless steels in sea water.

Widely used: **PREN = %Cr + 3.3 %Mo + 16 %N**

NACE formula **PREN = %Cr + 3.3 (%Mo + 0.5% W) + 16 %N**

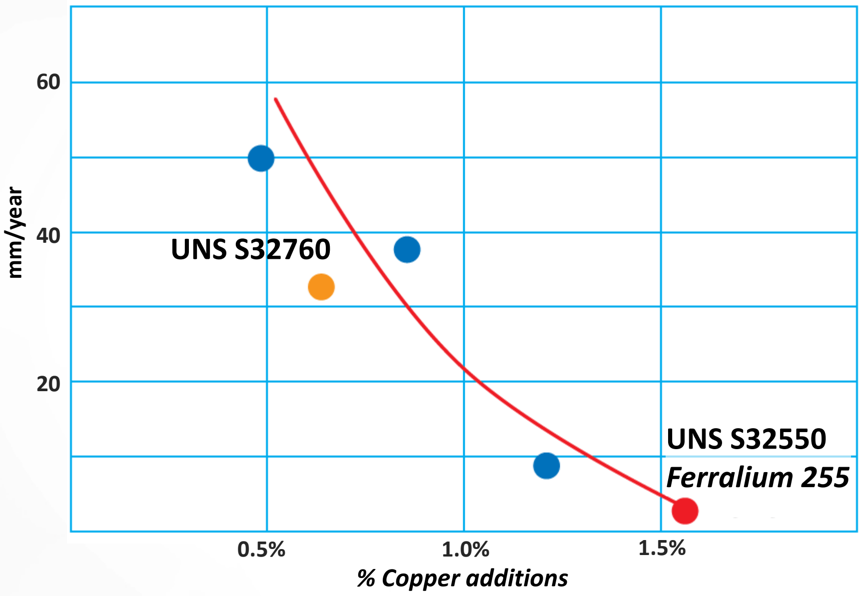
Developmental [1] **PREN = %Cr + 3.3 %Mo + 30 %N – 123 [%S + %P]**

Though useful, these indices are not directly indicative of corrosion resistance in H_2S-containing oil field environments.

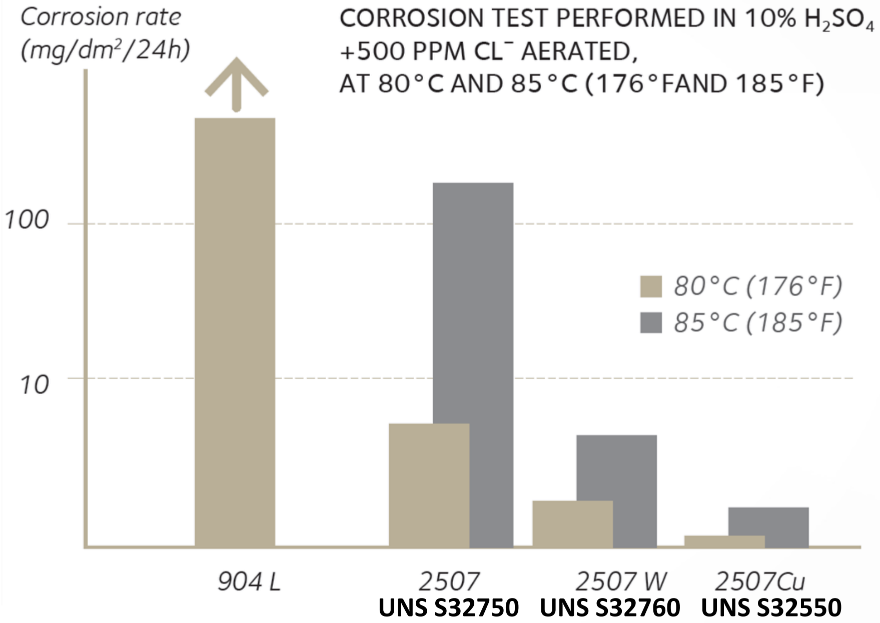
Similarly, they consider a benefit from only a handful of elements (Cu excluded).

[1] P. Combrade and J-P. Audouard, "Duplex Stainless Steels and Localised Corrosion Resistance“. Proceedings of the Duplex Stainless steel Conference, Beaune France, p. 257, Oct 1991

Published corrosion data – sulphuric acid

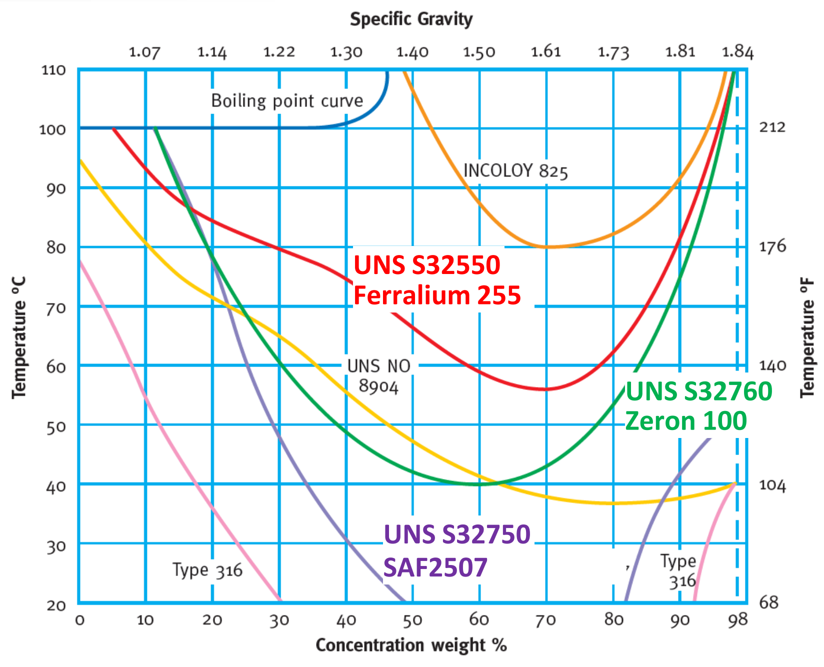


Mass loss in 70% sulphuric acid at 60°C.
Source: Langley Alloys



Mass loss in 10% sulphuric acid + 500ppm Cl- at 80/85°C.
Source: Industeel

Published corrosion data – sulphuric acid

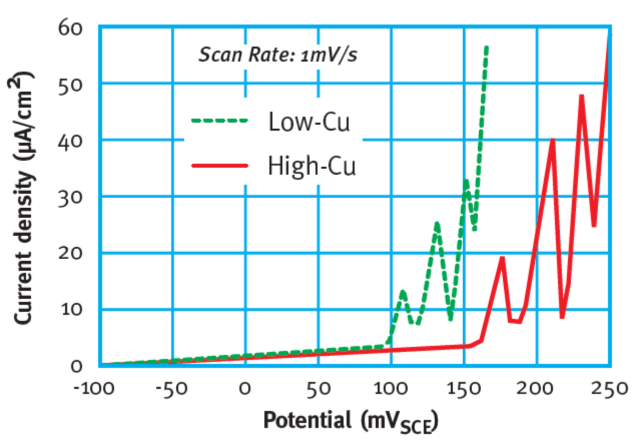


Source: Langley Alloys

Increased Cu content is widely-accepted to improve resistance to attack by acids, particularly sulphuric acid.

An example of another (unrelated) alloy containing Cu specifically for enhanced acid resistance is Alloy 20 (UNS S08020 / 2.4660) which contains 3-4% Cu.

Published corrosion data – Cl- solutions



Electrochemical Polarisation Curves in 3.5% NaCl at 65°C.
Low copper = 0.6%, High copper = 1.6%.
Source: Sykes/Garfias, University of Oxford

The current density trace for the high-Cu (1.6%) sample displays a lower passive current than that of the low-Cu (0.6%).

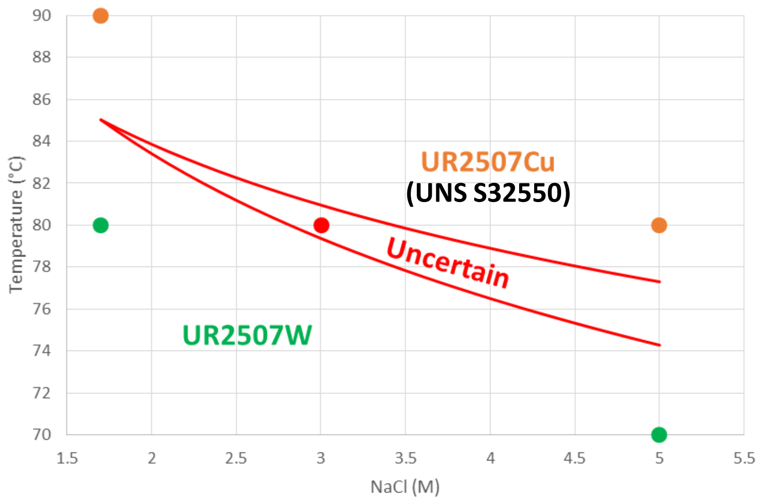
This suggests less likelihood of corrosion occurring in chloride environments.

nb. specific solution/temperature

Previous presentations results – SSW 2017

ArcelorMittal Industeel

"Influence of copper and tungsten addition on the passivity and on the pitting corrosion resistance of super duplex stainless steel"

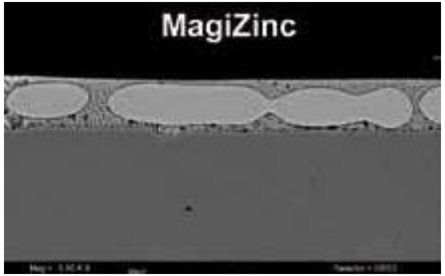


Cu-bearing SDSS (S32550) outperforms W-bearing SDSS (S32760) in more aggressive environments (higher temperatures, higher concentration of Cl^-).

Thicker passive film forms.

Affect appears to be dependent upon the pH of the local solution.

Academic partner – University of Swansea



Construction
- cut-edge corrosion of pre-painted Colorcoat roofing sheets

Automotive
- performance of new metallic coatings in customer applications

Previous contact from my work with Tata Steel, providing innovative support to product and process development.

Prof. Geraint Williams
School of Engineering

Jack Bonfield
M2A Masters Programme

Academic partner – project objectives

1) Gain greater insight into the passivation phenomenon from Cu and W additions

2) Identify conditions under which chosen alloy(s) provide enhanced performance

3) Optimise alloy additions based upon insight gained of passivation phenomenon

Spoiler Alert

Objectives may have been beyond an initial 1-year Master project !

Literature survey - Tungsten additions

"Tungsten has been stated to increase resistance to crevice corrosion in high temperature chloride solutions to levels above which crevice corrosion ordinarily starts." (1)

"Others argue that when added above a certain threshold, tungsten has a synergistic relationship with molybdenum." (2)

"Tungsten is thought to either enrich the passive oxide film as WO_3 or inhibit electrolyte from entering pits and crevices as dissolved tungstate WO_4^{-2} ions." (1)

"Various papers have suggested optimum corrosion performance with W additions of 2-3%." (3)

(1) Roscoe, C.V. and Gradwell, K.J. (1986). The history and development of duplex stainless steels. *Duplex Stainless Steel*,86, p.34.
(2) Haugan, E.B., Næss, M., Rodriguez, C.T., Johnsen, R. and Iannuzzi, M. (2016). Effect of Tungsten on the pitting and crevice corrosion resistance of type 25Cr super duplex stainless steels. *Corrosion*, 73(1), pp.53-67.
(3) Ogawa, K., Okamoto, H., Ueda, M., Igarashi, M., Mori, T. and Kobayashi, T. (1996). Effects of tungsten on pitting corrosion resistance and impact toughness in the HAZ of duplex stainless steel - study of weldability of high-tungsten duplex stainless steel (1st Report). *Welding International*, 10(6), pp.466-472.
(3) Jeon, S., Kim, S., Lee, I., Kim, J., Kim, K. and Park, Y. (2012). Effects of W substitution on the precipitation of secondary phases and the associated pitting corrosion in hyper duplex stainless steels. *Journal of Alloys and Compounds*, 544, pp.166-172.

Literature survey - Copper additions

"Alloys with increased Cu content showed higher pitting potentials in HCl and 3.5% NaCl solutions." (1)

"Beneficial effects of copper additions resulted from a synergistic effect of copper and nitrogen in the austenite phase and copper and molybdenum in the ferrite phase." (2)

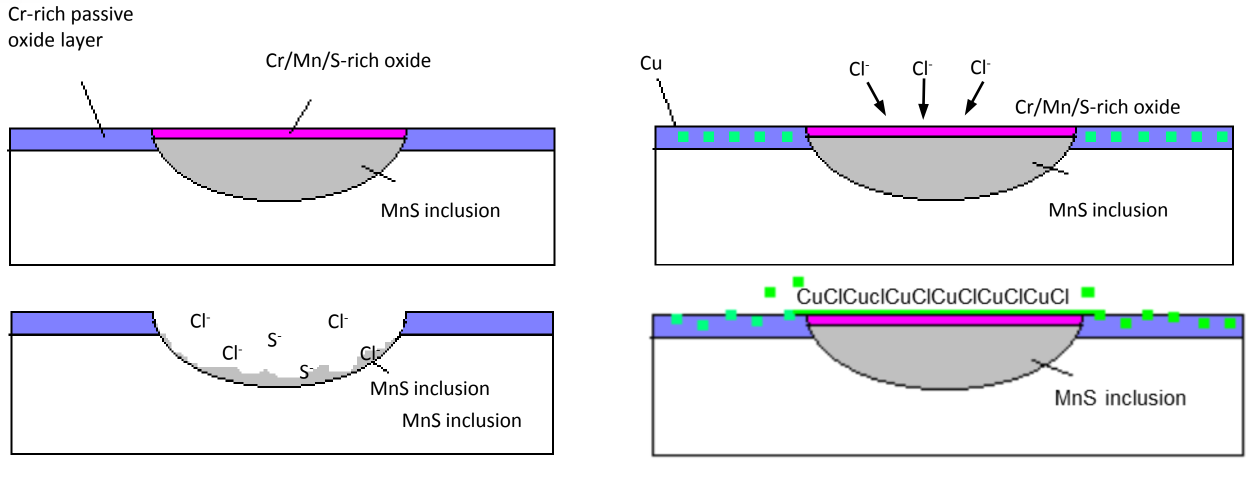
"Cu additions also improve resistance against Stress Corrosion Cracking, intergranular corrosion, and crevice corrosion." (3)

"Testing found copper additions to have a negligible or detrimental effect on corrosion resistance, decreasing the range of temperatures/concentrations where the alloy is passive in HCl and dilute sulphuric acid." (4)

(1) Garfias-Mesias, L. and Sykes, J. (1998). Effect of Copper on Active Dissolution and Pitting Corrosion of 25% Cr Duplex Stainless Steels. *CORROSION*, 54(1), pp.40-47.
(2) Combrade O., Audouard J.P., "Duplex stainless steels and localised corrosion resistance", Proc. Conf. Duplex stainless steels '91, France, Les Editions de Physique, 257-281, 1991.
(3) Ogura, S., Sugimoto, K. and Sawada, Y. (1976). Effects of Cu, Mo and C on the corrosion of deformed 18Cr-8Ni stainless steels in H2SO4/NaCl solutions. *Corrosion Science*, 16(5), pp.323-337.
(4) Kivisäkk, U.H. and Frodigh, J. (2013). Influence of Copper in Super Duplex Stainless Steels on Iso-Corrosion Curves in Hydrochloric Acid and Dilute Sulfuric Acid. In NACE International. [online] Orlando, Florida.

Literature survey – Copper additions

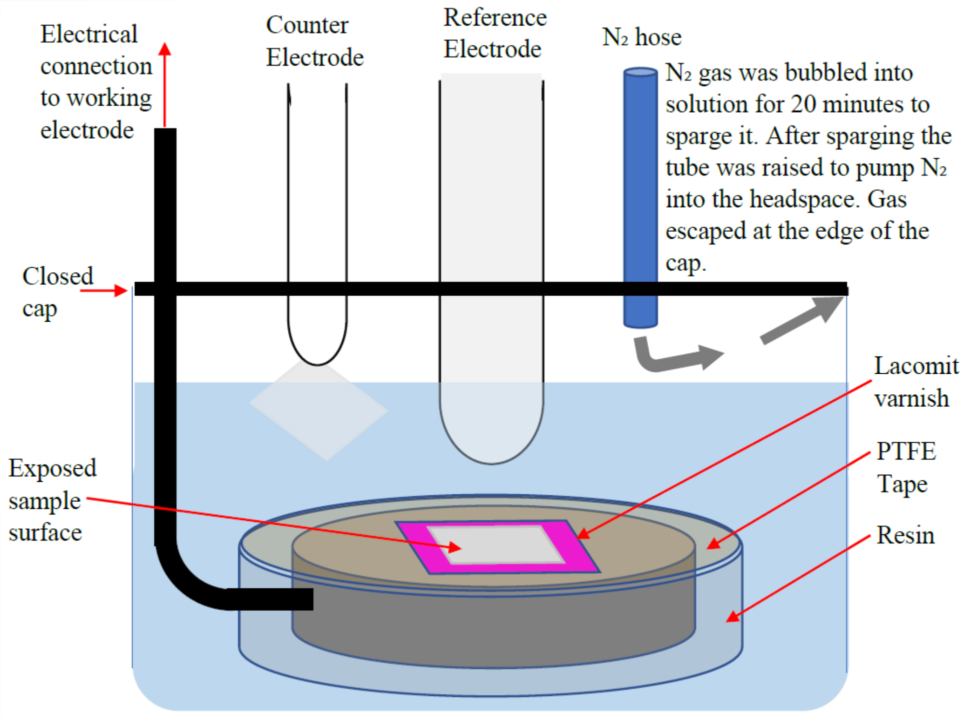
"Some sources agree that additions of Cu in acid results in benefits from the accumulation of metallic Cu on the surface which reacts with Chloride ions to form a protective insoluble salt film." [1]



A form of 'self-healing' protection, limiting the propagation of pitting after their initial formation ?

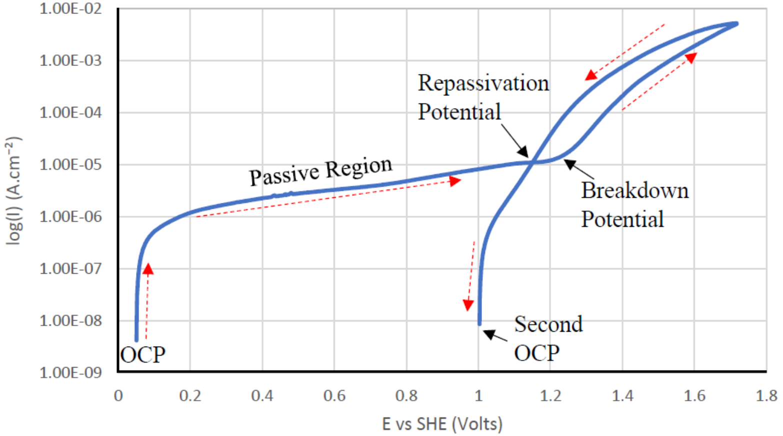
1) Garfias-Mesias, L. and Sykes, J. (1998). Effect of Copper on Active Dissolution and Pitting Corrosion of 25% Cr Duplex Stainless Steels. *CORROSION*, 54(1), pp.40-47.

Potentiodynamic Polarisation experiments



A standard electrochemical test, for which the most difficult challenge was cutting and polishing the SDSS samples (relative to materials normally examined within the laboratory !).

Potentiodynamic Polarisation experiments



Basic overview of the experiment

- begins at the open circuit potential (OCP)
- potential is gradually increased
- stop when a current of value 0.005 ($A.cm^{-2}$) is reached
- potential is reversed and is gradually decreased

1) **passive region** indicates metastable pitting

2) **stable pitting** is observed > **breakdown potential** (Eb)

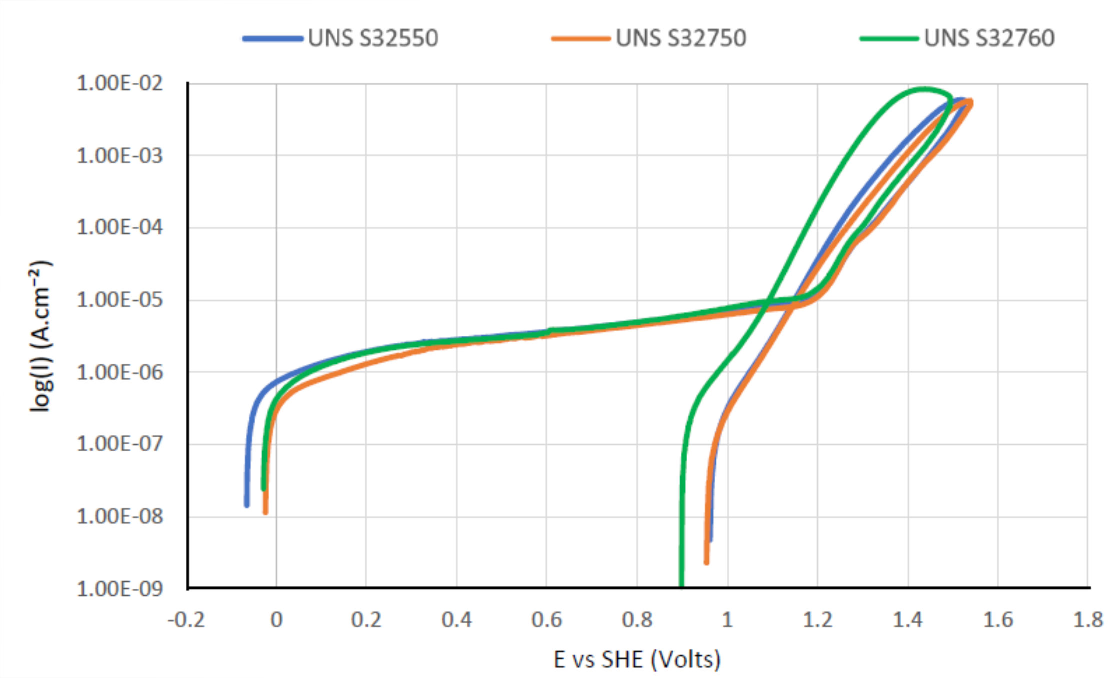
3) on the return sweep a hysteresis loop is formed

   a) a narrow or no loop indicates rapid re-passivation

   b) a wide hysteresis loop indicates slow or incomplete re-passivation

4) the closer the second OCP is to the initial OCP potential value indicates worse repassivation properties

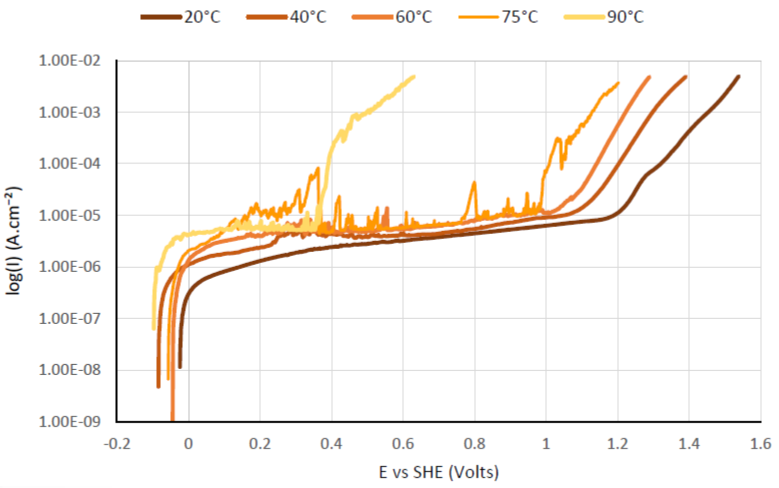
Potentiodynamic Polarisation experiments



Repassivation sweeps in 0.6M NaCl solution at pH 8.0 at 20°C

At lower temperatures, S32550 & S32750 appear to re-passivate more quickly, witnessed by the narrower hysteresis loops than for S32760.

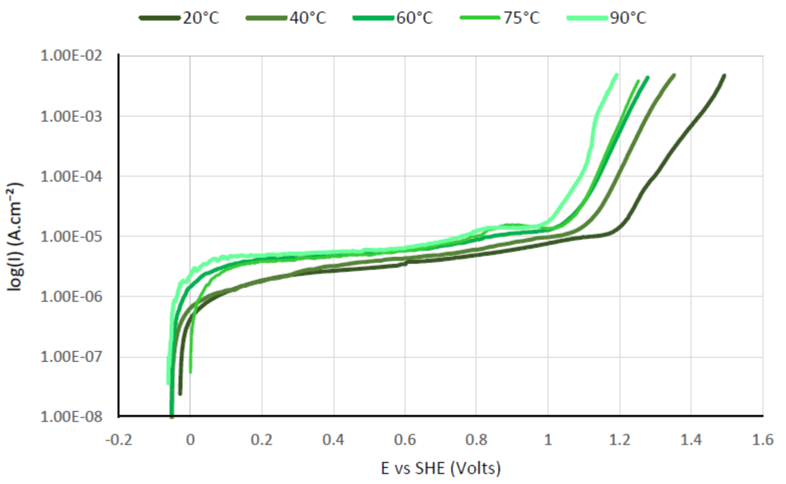
Potentiodynamic Polarisation experiments



anodic going sweeps in 0.6M NaCl solution at pH 8.0

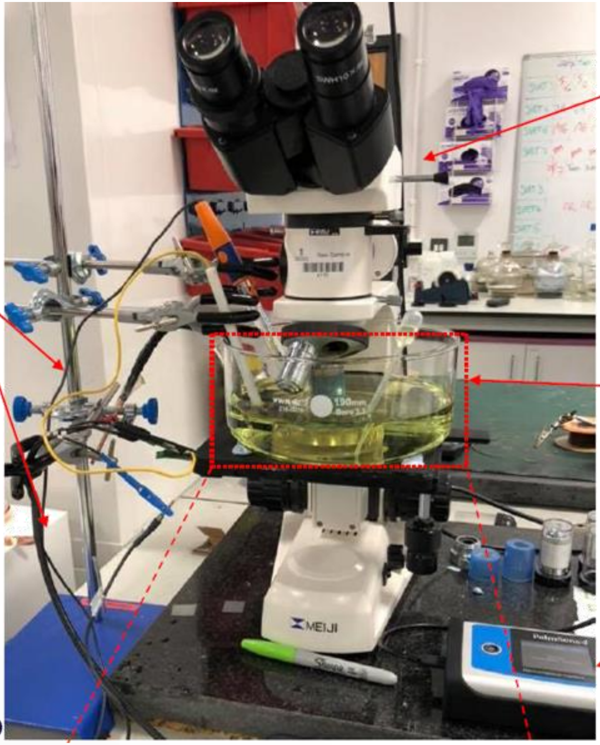
← S32750

S32760 →

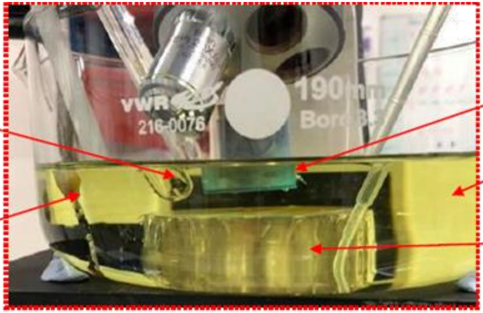


However, at higher temperatures (75°C & 90°C) then S32760 appears to suffer less pitting than either S32550 or S32750.

Time Lapse Microscopy experiments

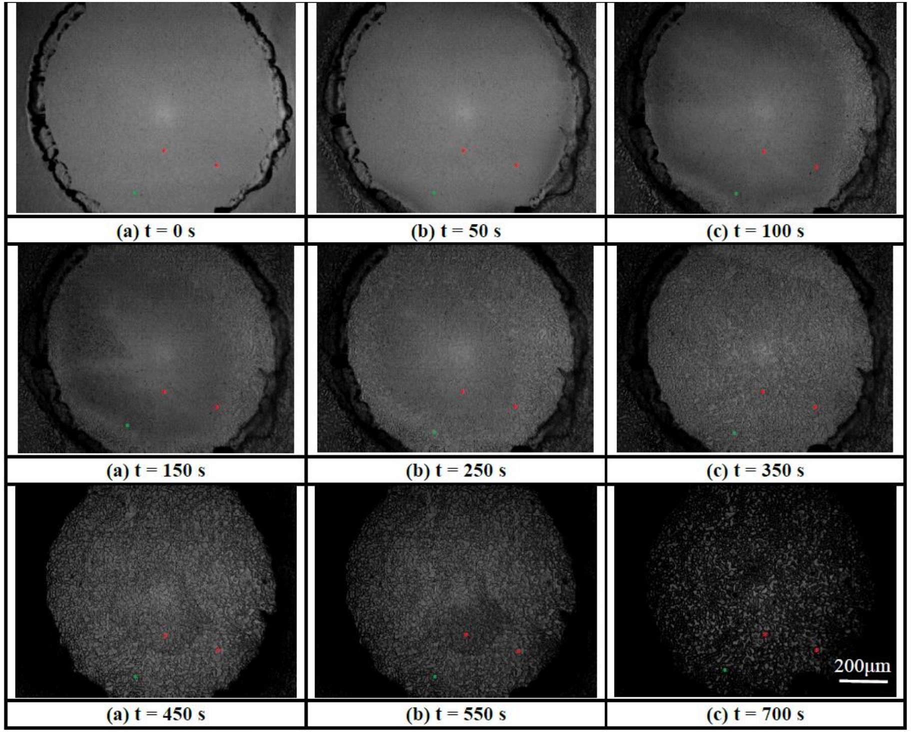


(a)



(b)

Time Lapse Microscopy experiments



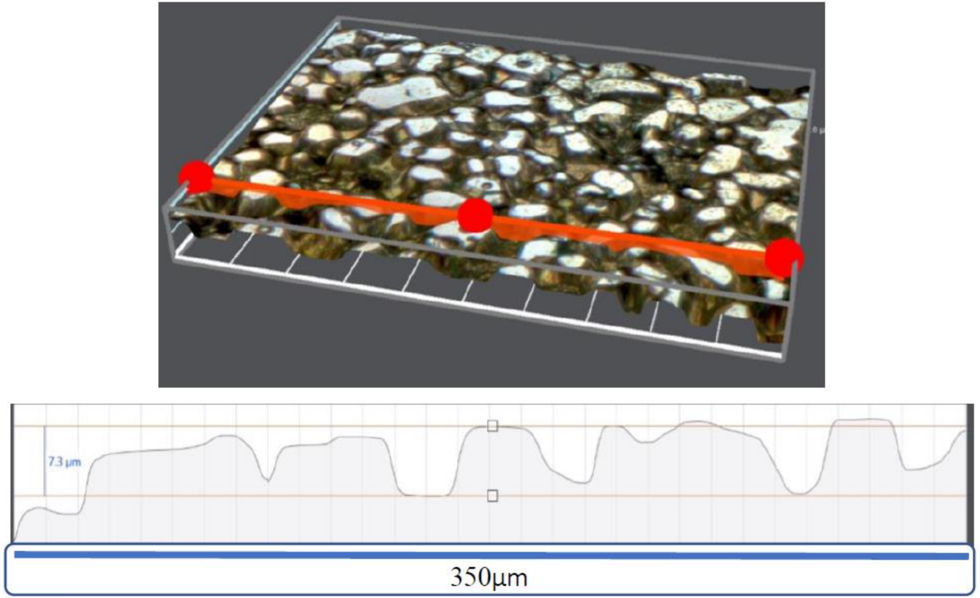
S32550 polarised at 1.25V in 0.6M NaCl solution at pH 5.7 at room temperature.

An initial 'look-see' of the different alloys performance at one very specific set of conditions.

All samples suffered selective attack of the ferrite phase.

S32760 reached steady-state corrosion first, then S32550 and finally S32750.

Time Lapse Microscopy experiments



3D profile of UNS S32750 microstructure after polarisation at 1.25 Volts during TLM experiments with a height profile taken from the trend line.

Microstructural profiles confirmed the extent of the selective attack of the ferrite phase.

< CPT = selective attack

> CPT = stable pitting

Chlorine concentration only becomes more significant at higher temperatures due to the different form of corrosion.

Conclusions

i. Different SDSS alloys performance varies in specific mediums/conditions

ii. Literature reviews provide conflicting evidence on the merits of Cu & W additions

iii. University of Swansea possess a number of innovative analysis techniques

iv. Results to date (in artificial seawater) suggest that

    i. S32550 & S32750 perform better at lower temperatures

    ii. S32760 performs better at higher temperatures

v. This somewhat conflicts with results presented at this event in 2017

vi. The initial one-year project has been repeated for a second term