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EFFECT OF MICROSTRUCTURE AND SURFACE FINISH ON LOCALIZED CORROSION PERFORMANCE OF SUPER DUPLEX STAINLESS STEEL IN SEAWATER

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PREFACE

This master thesis was carried out as a part of a project run by NTNU and GE Oil & Gas. Corrosion tests of Super Duplex Stainless steel at different temperatures were performed at then NTNU/SINTEF Corrosion Lab.

I would like to thank Professor Roy Johnsen at the Materials Department of at NTNU for his excellent guidance and encouraging and welcoming atmosphere whenever needed. I'm impressed by his capacity and availability at all times despite a very busy schedule.

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Monika Næss

ABSTRACT

Corrosion resistant alloys (CRAs) used in subsea pressure-retaining components must be compatible with production fluids and resistant to pitting and crevice corrosion in seawater. Whereas materials selection in production environments is governed by well-established international standards such as ISO 15156, much debate still exists as of how to determine the seawater localized corrosion resistance of higher grade CRAs such as duplex super duplex stainless steels (DSS and SDSS, respectively).

While most industry specifications rely on the ASTM G48 standard to determine localized corrosion resistance, for duplex and super-duplex stainless steels there is no consensus on surface finish prior testing (e.g. polishing or pickling) and test temperature (e.g. 50 °C in NORSOK 630 versus 40 °C in ASTM A923). Moreover, it is unclear whether existing procedures are sensitive enough to determine the onset of deleterious phases such as σ-phase and chromium nitrides.

The objective of this investigation was to quantify the seawater pitting corrosion resistance of a type 25Cr SDSS (UNS S32750) and its correlation with microstructure and surface finish before testing. Cyclic potentiodynamic polarization (CPP) testing was used to determine the effect σ-phase on the corrosion response of the system. CPP results were then compared against industry standard practices based on the ASTM G48 Method A test.

In addition, CPP tests were conducted at various temperatures, ranging from 25 to 90°C, to determine the effect of deleterious phases on critical pitting temperature (CPT) and overall localized corrosion resistance.

The results from this project indicate that the Critical Pitting temperature for standard solution annealed Super Duplex Stainless Steel is 60-70°C. It is also shown that the corrosion resistance is reduced for material that contains sigma phase showing a Critical Pitting Temperature of 40-50°C. The surface treatments seem to have less effect on the values, but pickled surfaces gave a more repeatable result.

CONTENTS

ABBREVIATIONS

ASTM - American Society for Testing and Materials

CPP - Cyclic Potentiodynamic Polarization

CPT – Critical Pitting Temperature

Cr – Chromium

CRA – Corrosion Resistant Alloys

DSS – Duplex Stainless Steel

EOR – Enhanced Oil Recovery

HF - Hydrofluoric Acid

HNO_3 – Nitric Acid

IPM – Department of Engineering Design and Materials

IPK – Department of Production and Quality Engineering

Mo – Molybdenum

N – Nitrogen

NaCl – Sodium Chloride

Ni - Nickel

NORSOK - Norsk Sokkels Konkurranseposisjon

OCP – Open Circuit Potential

PREN – Pitting Resistance Equivalent Number

SCE – Saturated Calomel Electrode

SS – Stainless Steel

SDSS – Super Duplex Stainless Steel

1 INTRODUCTION AND EXPERIENCE FROM AVAILABLE LITERATURE

1.1 BACKGROUND

Corrosion resistant alloys (CRAs) used in subsea pressure-retaining components must be compatible with production fluids and resistant to pitting and crevice corrosion in seawater. Whereas materials selection in production environments is governed by well-established international standards such as ISO 15156, much debate still exists as of how to determine the seawater localized corrosion resistance of higher grade of Corrosion Resistant Alloys (CRAs) such as duplex super duplex stainless steels (DSS and SDSS, respectively).

While most industry specifications rely on the ASTM G48 standard to determine localized corrosion resistance, for duplex and super-duplex stainless steels there is no consensus on surface finish prior testing (e.g. polishing or pickling) and test temperature (e.g. 50 °C in NORSOK 630 versus 40 °C in ASTM A923). Moreover, it is unclear whether existing procedures are sensitive enough to determine the onset of deleterious phases such as σ-phase and chromium nitrides.

The objective of this investigation was to quantify the seawater pitting corrosion resistance of a type 25Cr SDSS (UNS S32750) and its correlation with: i) alloy's microstructure and ii) surface finish before testing. Cyclic potentiodynamic polarization (CPP) testing was used to determine the effect of the presence of σ-phase on the corrosion response of the system. CPP results were then compared against industry standard practices based on the ASTM G61 Method A test. In addition, CPP tests were conducted at various temperatures, ranging from 25 to 90°C, to determine the effect of deleterious phases on critical pitting temperature (CPT) and overall localized corrosion resistance.

1.2 DUPLEX STAINLESS STEELS

An overview of Duplex stainless steels (DSS) are given by J.O. Nilsson [1]

Duplex Stainless Steels may be defined as a family of steels having a two phase ferritic-austenitic microstructure, the components of which are both stainless, i.e. contain more than 13%Cr. In practice, the term DSS is reserved for alloys in which ferrite and austenite are present in relatively large separate volumes and in approximately equal volume fractions, as opposed to alloys in which one constituent appears in the form of small precipitates. When the DSS were compared with austenitic steels several advantages became apparent, namely, higher mechanical strength, superior resistance to corrosion, and a lower price because of the low nickel content. It was later realised that advantages could be obtained from the use of DSS in environments where, owing to stress corrosion cracking, standard austenitic steels were inappropriate.

The interest in DSS in recent years derives from the high resistance of high alloy DSS to chloride induced corrosion, which is a problem of major concern in many marine and petrochemical applications. Perhaps even more important are the great improvements in weldability achieved by reducing the carbon content and increasing the nitrogen content. An attractive combination of corrosion resistance and mechanical properties in the temperature range - 50 to 250°C is offered by DSS. For example, the resistance to stress corrosion cracking and pitting corrosion is excellent and in many cases superior to that of standard austenitic steels of comparable cost. Owing to the fine grained structure yield strength values typically twice those of austenitic grades are obtained in the annealed material state without any substantial loss in toughness. It is important to stress, however, that DSS are less suitable than austenitic steels above 250°C and below - 50°C because of the brittle behaviour of ferrite at these temperatures.

A factor of economic importance is the low content of expensive nickel, usually 4-7% compared with 10% or more in austenitic grades, as a result of which the life cycle cost of the DSS is the lowest in many applications.

There has been an increased use of nitrogen as an alloying element, stabilising austenite and therefore replacing nickel in this respect. As a result of this, austenite reformation during welding has become more rapid and in addition improved corrosion resistance, in particular resistance to pitting corrosion, have been obtained.

The use of stainless steels and other corrosion resistant materials in corrosive environment has increased drastically over the last 30 years. The development of high strength materials with good weldability and corrosion resistance contributes to weight reduction, reduced maintenance activities and they have a nice and smooth surface finish that is easy to keep clean.

Super duplex is by definition a duplex stainless steel with a Pitting Resistance Equivalent Number (PREN) ≥ 40.

$PREN = \%Cr + 3.3\%Mo + 16\%N$

Some include the content of Tungsten also in the formula giving the following expression:

$PREN = \%Cr + 3.3 (\%Mo + 0.5\%W) + 16\%N$

Most super duplex grades have 25% chromium or more. The most common grades are S32760, S32750 and S32550. [2] The composition and main characters are listed in Table 1

Table 1 Composition of Super Duplex

UNS	Material	Fe	Cr	Ni	Mo	N	Other
S32550		Bal	25	5,5	3,5		
S32750*	SAF 2507	Bal	25	7	3,5	0,27	Co(1,0)
S32760		Bal	25	7	3,5		

** Material used in this thesis*

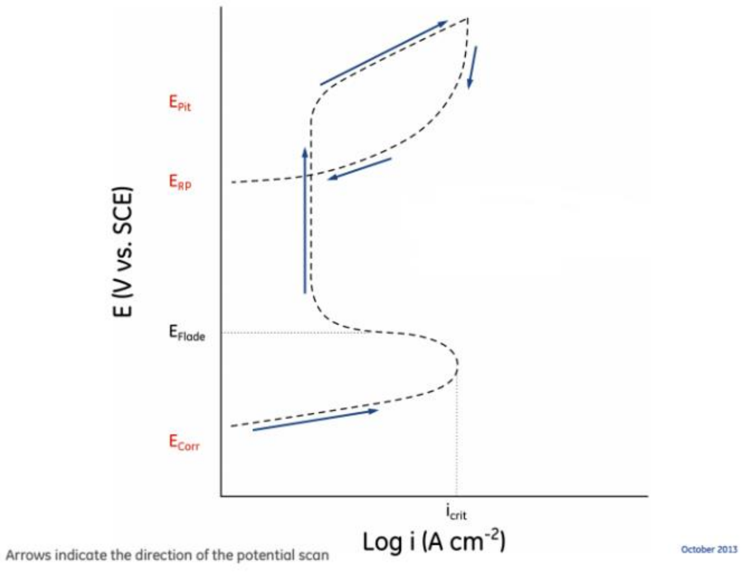
According to NORSOK M-001 25Cr Duplex stainless steel cannot be used in seawater above 20°C however this requirement is based on chlorinated seawater since most seawater for process use is chlorinated. [2].

1.3 PITTING CORROSION AND POLARIZATION CURVES

Pitting corrosion occur on passive metals and alloys in corrosive environment containing chlorine, bromine, iodine or perchlorate ions when the potential exceed a critical value called the Pitting Potential. This limit is depending on many different factors e.g. pH, temperature, oxide layer, electrolyte composition, flow rate, surface finish and microstructure. [3]

The Open Circuit Potential (OCP) will be different for different environments. This is the potential that is natural for an alloy in an electrolyte without applying any potential.

Traditionally the PREN has been used to compare different alloys and their resistance to pitting corrosion. However this is not sufficient to fully describe or evaluate the pitting resistance of a material as there are many other factors than chemical composition that affects the pitting resistance of a material. An alternative way of describing the resistance to pitting corrosion is to evaluate the difference between Pitting Potential (E_P)$_{)}$, Re-passivation Potential (E_{RP}) and Corrosion potential (E_{CORR}). The alloy can be considered seawater resistant if E_{RP}-$E_{CORR} > 200$mV [4]. These parameters can be determined by running a cyclic polarization scan. A typical plot from such a scan is shown in the schematic in Figure 1.



Arrows indicate the direction of the potential scan

October 2013

Figure 1 Typical cyclic polarization scan [5]

E_P is defined as the least positive potential at which pits can form. E_{REP} is the potential where the material comes back to a passive state after pits have been formed.

There are several ways of defining the critical potentials when running cyclic polarization scans. For this project the Pitting potential (E_P) is defined as the inflection point as shown in Figure 2 below. It is the point where a sharp increase in current density occurs. Notice that in this plot, the current density is plotted on the vertical axis and the potential on the horizontal axis.

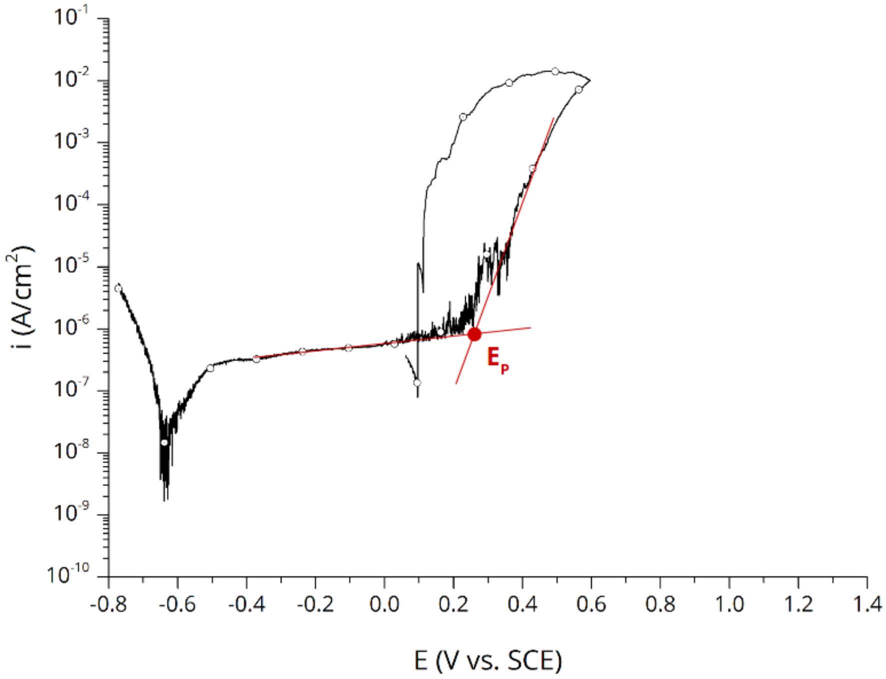


Figure 2 Definition of pitting potential [5]

The Repassivation potential (E_{RP}) is defined as the potential where the current density is below 2µA/cm^2 as shown in Figure 3

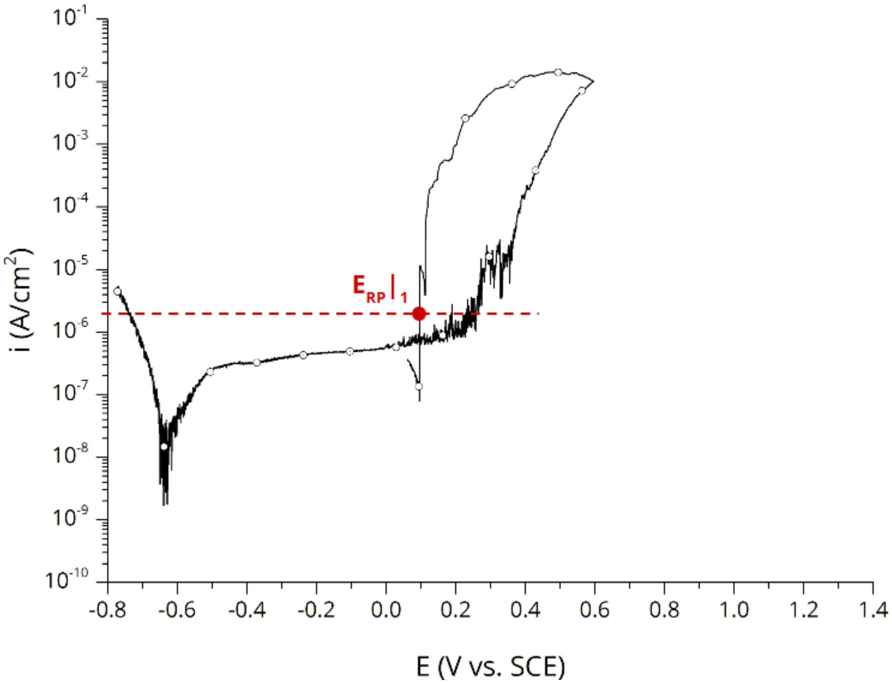


Figure 3 Definition of Repassivation Potential [5]

For conditions where the steel show transpassive behaviour and therefore has no clear pitting potential the transpassive potentials are measured at the inflection point as shown in Figure 4. In these cases the transpassive potential is reported instead of the pitting potential.

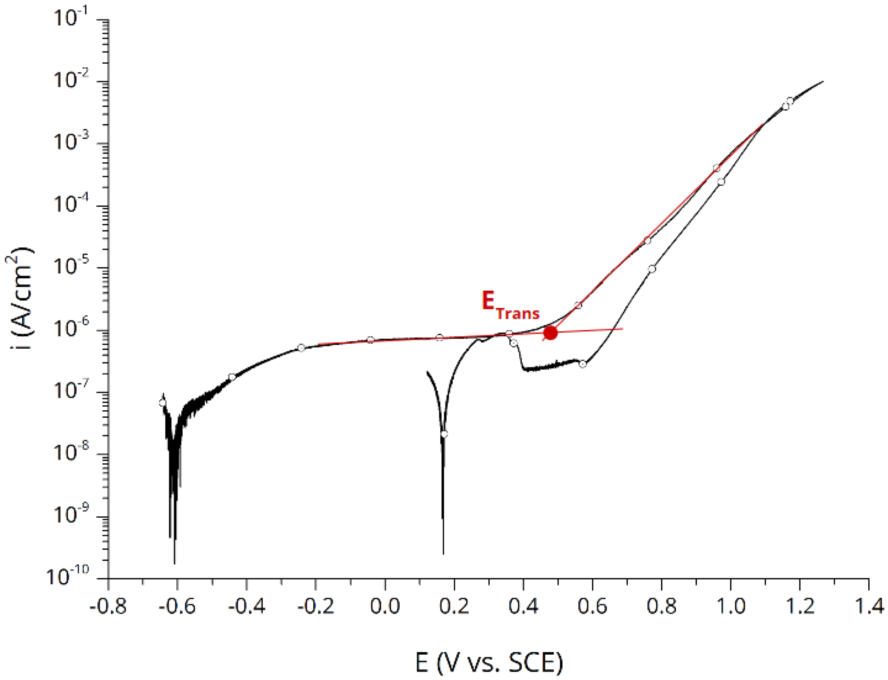


Figure 4 Definition of Transpassive Potential [5]

The Passive Current Densities (i_{pass}) are defines as the average or midpoint of the current density in the passive state. This is shown in Figure 5

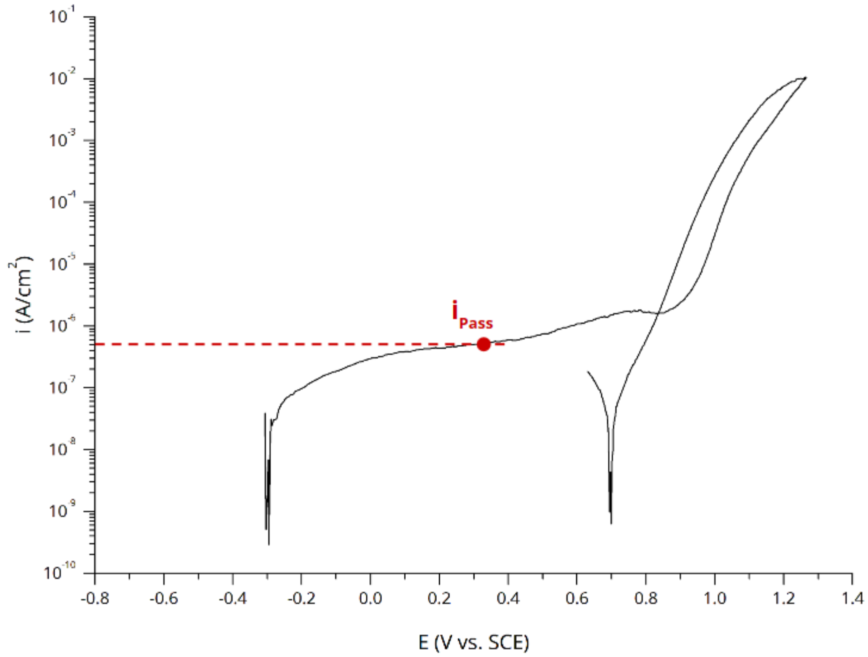


Figure 5 Definition of Passive Current Density

1.4 CRITICAL PITTING AND CREVICE TEMPERATURE

The Critical Pitting Temperature (CPT) and the Critical Crevice Temperature (CCT) have been investigated by many researchers over the years, but for such complex forms of corrosion with many parameters, the values seem to vary. CPT is the temperature where the pitting is likely to initiate and it can be found in many different ways. The most common one is by using a standard method like the one described in ASTM standard G48 E [6] or similar. It can also be found by evaluating an E_P vs Temperature plot as done in this project.

CCT is dependent on the repassivation properties of a material. E_{RP} is a measure of the susceptibility of a material to localized corrosion. E_{RP} is related to the repassivation of growing pits. In the "deep pit condition", a growing pit can be visualized as a special case of crevice corrosion. Early work correlated crevice corrosion resistance with E_{RP} of lower grade stainless steels.

By measuring Repassivation potential (E_{RP}) vs Test temperature (T) we can infer a critical temperature, which could be associated with the initiation of crevice corrosion. [7]

Some of the CPT and CCT values given by the suppliers of steel are presented in Table 2. The test methods are not given for all values, but it gives an indication of how much the results are varying. The values given by the suppliers and the critical temperatures given in the literature show that there are no common temperature limit for Super Duplex SS in seawater defined. See table 2-4.

Table 2 Critical Pitting and Crevice Corrosion Temperatures grade UNS S32750

SUPPLIER	CPT [°C]	CCT [°C]	REFERENCES
SANDVIK	80 (ASTM G48)	50	Appendix C
OUTOKUMPU	84±2 (ASTM G150) 65 (ASTM G48)	35	[8]
LANGLEY ALLOYS	>50 (ASTM G48)	-	[9]
SANDMEYER STEEL	>95 (1M NaCl)	42 (10% $FeCl_3$)	[10]

From available literature some other values are found.

A. B. Høydahl [11] did research on crevice corrosion at different potentials. The different potentials represent different environments and chloride contents. The results are listed in Table 3. The experiments were done on a slightly different type of Super Duplex SS namely UNS 32760 that contains some extra alloying elements like Copper (Cu) and Tungsten (W) compared to UNS S32507.

Table 3 Measured CCT and weight loss of UNS S32760 at different potentials [11]

POTENTIAL [V*]	CCT [°C]	REMARK
+0,250	> 92	No corrosion occurred
+0,300	89±1	Potential area for OCP with normal biofilm
+0,350	73±1	Potential area for OCP with normal biofilm
+0,400	49±1	Potential area for OCP with normal biofilm
+0,500	61±1	
+0,550	63±1	
+0,600	51±1	Corresponds to OCP in presence of chlorine

**Ag/AgCl Reference electrode*

Other critical temperatures collected from available literature are listed in Table 4.

Table 4 CPT and CCT from previous research

STEEL GRADE	CPT	CCT	TEST METHOD	REFERENCE
UNS S32507	78	38	ASTM G48	[12]
UNS S32507		50 30(welded)	CrevCorr Artificial seawater	[13]
UNS S32507	82	68	Potensiostatic test 700mV Ag/AgCl	[14]
UNS S32750	87,6	-	Potensiodynamic test 1M NaCl	[15]
UNS 32507	80±5	-	ASTM G48	[1]

1.5 EFFECT OF MICROSTRUCTURE

Super Duplex Stainless Steel has a microstructure consisting of the two phases Austenite and Ferrite. If the heat treatment is not performed correctly some unwanted secondary phases can be formed. See Figure 7 for the Temperature-Time-Transformation (TTT) diagram for Super Duplex SS.

Formation of precipitates changes the properties of the material. Higher Cr and Mo content promotes the precipitation of phases such as σ (Sigma), χ (Chi) and α' (alpha prime) when exposed to temperatures of 300°C and 900°C. Above all the σ -phase is considered to be the most detrimental phase in Super Duplex Stainless Steels. It affects the mechanical properties by making the material more brittle and weaker. The phase depletes Cr and Mo from the surrounding phases leading to a reduction in corrosion resistance. It has been shown from potential and current transients that the alloy became susceptible to pitting when σ phase was present. [16] This effect is investigated further in this master thesis.

Bastos et al. [17] performed pitting corrosion tests of samples with and without phase precipitates in a Sodium Chloride (NaCl) solution at 25°C, 60°C and 90°C. The results of their anodic polarization are shown in Figure 6. Sample A was not heat treated, Sample B had been heat treated for 15 minutes at 800°C and Sample C for 2 hours at 800°C.

The figures show that the corrosion current density is strongly dependent on the microstructure and on temperature. The samples with secondary phase precipitates reach the current limit criterion of $3mA/cm^2$ at very low potentials even at low temperatures. These samples also show a less smooth curve indicating less homogenous electrode reactions than the untreated sample. [17]

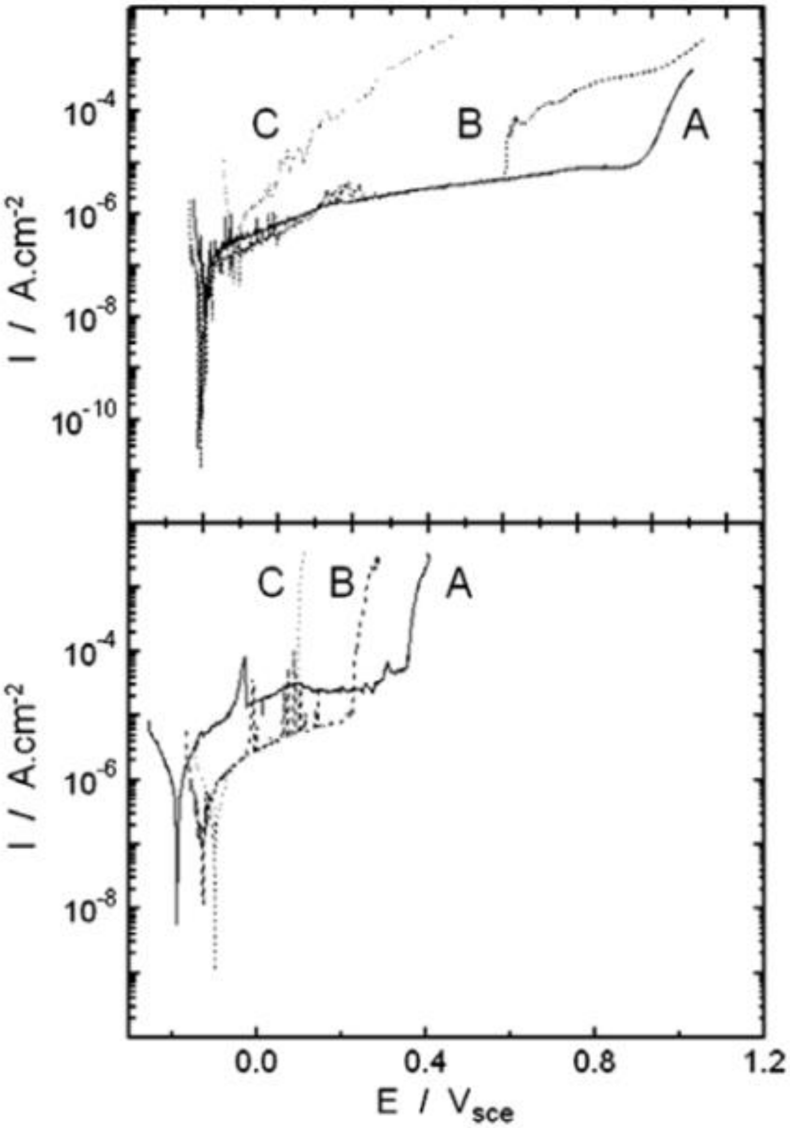


Figure 6 Polarization curves at 25 (top) and 90° C (bottom) after immersion for 30 min.

The TTT diagram for Super Duplex Stainless Steel (Grade SAF 2507) is shown in Figure 7. [1] The TTT diagram shows at what temperatures and exposure time the different phases and precipitates are formed. The heat treatment used for this project is marked with red arrows; 875°C for 7 minutes, then quenched in water to room temperature.

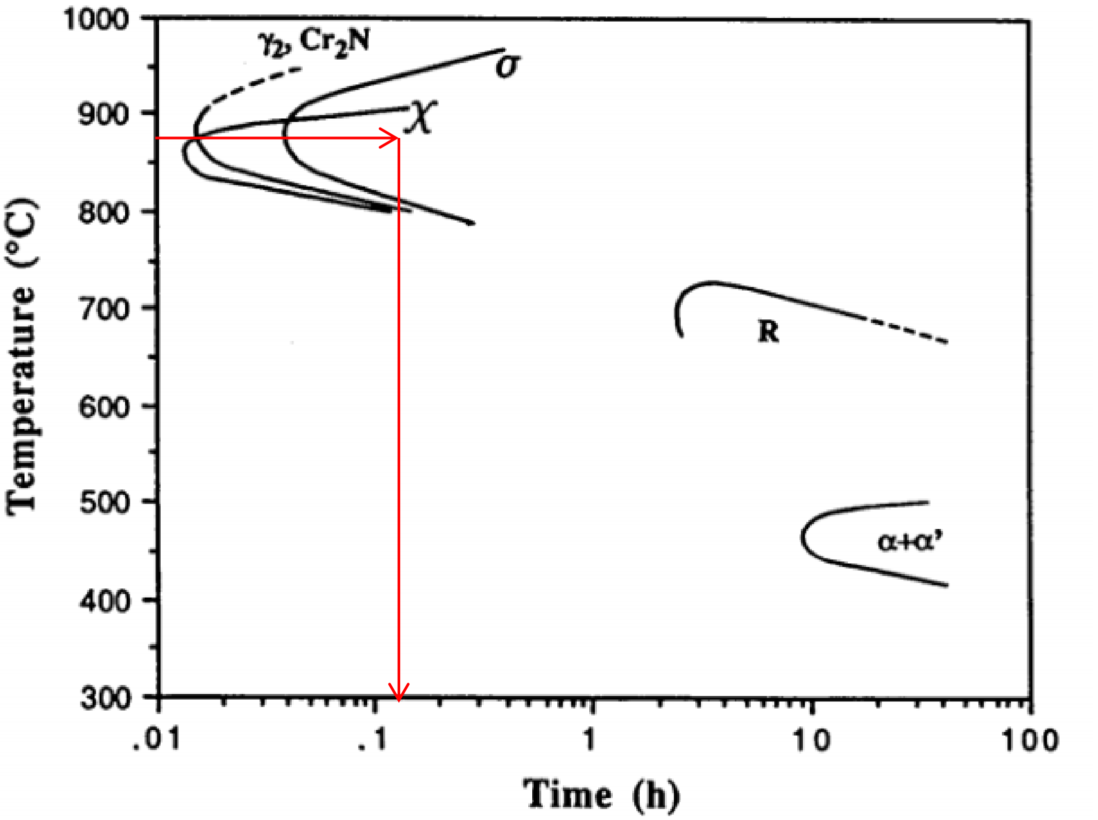


Figure 7 Temperature - Time - Transition Diagram for Super Duplex Stainless Steel [1]

1.6 THE EFFECT OF ALLOYING ELEMENTS

The different alloying elements are added to the steel to give the steel its mechanical and chemical properties. The amount of the different elements in addition to the fabrication process will determine the materials strength, ductility, microstructure, temperature resistance, weldability and corrosion properties. For Super Duplex SS the following alloying elements are the most relevant.

Chromium (Cr)

Chromium (Cr) is one of the main alloying elements in stainless steels. It is a ferrite former and at concentrations above 12% it can make a stable passive film on the metal surface. Increasing the Cr content up to 30% gives a better corrosion resistance, however at higher concentrations the risk of getting unwanted precipitates and change in mechanical, forming and welding properties. Adding other alloying elements to improve the chromium oxide film performance is therefore recommended instead of adding more chromium. [18]

Nickel (Ni)

Nickel (Ni) improves the chromium oxide and has good repassivation properties. It stabilizes Austenite and the amount of Ni required to retain the austenite structure is decreasing with increased Carbon content in the steel. Nickel improves the ductility at low temperatures and increases the resistance against acids. [18]

Molybdenum (Mo)

Molybdenum (Mo) is added to the steel to improve the resistance against localized corrosion such as pitting or crevice corrosion. Mo increases the strength of the passive layer by creating a layer of MoO_4^{2-} at the surface. The negative Cl^- ions will be repelled and will not have access to the surface to degrade the oxide layer. Mo is also a ferrite former. [18]

Nitrogen (N)

Nitrogen (N) is an austenite stabilizer and it increases the concentration of Mo at the surface. This is due to ammonium ions that lower the pH at the surface causing increased formation of MoO_4^{2-}. Nitrogen improves the weldability of duplex stainless steels and can have a positive effect on avoiding hydrogen embrittlement. Ni increases the resistance against localized corrosion at concentrations up to 0,25%. At higher concentrations the material becomes more brittle. [18]

Tungsten (W)

Addition of Tungsten (W) to Super Duplex SS show increased resistance to pitting and stress corrosion with the ratio of W to Mo content. The rate of embrittlement and the nucleation and growth of the σ phase due to aging is significantly delayed with increased W content. [19]

1.7 SURFACE FINISH

The exact condition of a surface can have a large influence on the pitting initiation and growth of a material. In general, samples prepared with a rough surface finish are more susceptible to pitting and has a lower pitting potential. For stainless steels heat treatment, polishing and abrasive blasting have been reported to decrease the pitting resistance, whereas pickling with Nitric and Hydrofluoric Acid is beneficial. [20] A smooth and clean surface will have less initiation points where pitting can occur.

The more homogenous the surface is, both chemically and physically, the higher the pitting potential, the lower the pit number and the better resistance to pitting corrosion. The effect of roughness on the pitting potential has been well documented. Surface treatments like polishing or chemical treatment in HNO_3 with additions of H_2SO_4, HF or

HCL will increase the pitting potential due to a smooth metal surface, removal of sulfide inclusions and enrichment of chromium in the stainless steel surface. [21]

There is not a lot available literature describing the difference of pickled and non-pickled surfaces. It might be because the difference is not very clear and there are other parameters like surface roughness that will have a larger influence on the corrosion properties.

2 EXPERIMENTS

To investigate the corrosion properties of Super Duplex SS experiments were performed according to the following procedure. The objective was to quantify the seawater pitting corrosion resistance of Super Duplex SS and its correlation with microstructure and surface finish.

The experiments were carried out at NTNUs corrosion lab at IPM in January to March 2014. The material that was tested was a sample of UNS S32570. See Appendix A for chemical composition and mechanical properties.

2.1 TEST PROCEDURE

1. The sample material was provided by GE Oil & Gas. Composition and mechanical properties are given in the Material Data Sheets in Appendix B.
2. The samples were machined at the workshop at NTNU, department of production and quality engineering (IPK) according to Figure 10
3. A total of 64 samples were tested according to the conditions presented in Table 2 below.
4. 32 of the samples were heat treated prior to testing to simulate poor heat treatment causing σ phase precipitation. These samples were put into the furnace at 875°C and kept there for 7 minutes before they were quenched in water. See Figure 7 for TTT diagram. The furnace used was a Nabertherm N 17/HR at the heat treatment laboratory at NTNU.
5. The micro structure was revealed by polishing and etching as described in ASTM A-923 and the precipitates were counted according to ASTM E562. The standards are described in section 2.2.
6. The surfaces of all samples were polished with SiC paper grade 600 and rinsed in ethanol in an ultrasonic bath for 5 minutes.
7. 32 of the samples were pickled according to NORSOK M-630. [22] The samples were lowered into a solution of 20% Nitric Acid (HNO_3) and 5% Hydrofluoric Acid (HF) at a temperature of 60°C and kept there for 5 minutes. Special safety procedures for handling HF were followed.
8. The surface roughness was measured on some of the samples. There was no clear difference in surface roughness for the pickled or non-pickled samples. The values were in the range of R_a ~2,5µm
9. After the polishing and/or pickling the samples were rinsed in distilled water and left in a desiccator for minimum 24h prior to testing.

10. The samples were connected to the potentiostat by platinum thread. The potentiostat used was a Gamry Interface 1000 connected to a computer with Gamry software. Two samples were run in parallel in different
11. 3,5 wt. % NaCl solution was used as electrolyte and heated to the given test temperature by a hot plate connected to a thermostat.
12. pH of the electrolyte was measured before and after the test by a calibrated pH meter.
13. The electrolyte was connected to a calibrated SCE reference cell using a tube filled with electrolyte and a cotton string to provide constant connection (salt bridge). The reference cell was filled with saturated Potassium Chloride (KCl) solution.
14. The sample was lowered into the electrolyte when the electrolyte was at test temperature.
15. The OCP was measured for one hour before the polarization scan. During this hour Nitrogen gas was used for purging to remove the oxygen in the solution. The purging continued during the whole test.
16. The sample was polarized at a rate of 600mV/h from OCP until the current density reached the limit of 5mA/cm^2 was reached. Then the potential was brought back down at the same rate. Most of the samples were brought back to OCP, but some scans were stopped a bit earlier when assured that the repassivation potential was reached.
17. The samples were rinsed in water and pictures were taken and stored. The pictures are found in Appendix C
18. Some of the samples were examined in a microscope to evaluate the corrosion and surface after testing. The samples were examined first and then polished slightly with 3µm diamond suspension to reveal the pits and to remove the oxides. Then they were examined in the microscope again to confirm if pitting had occurred.
19. The data from the tests was stored and evaluated.

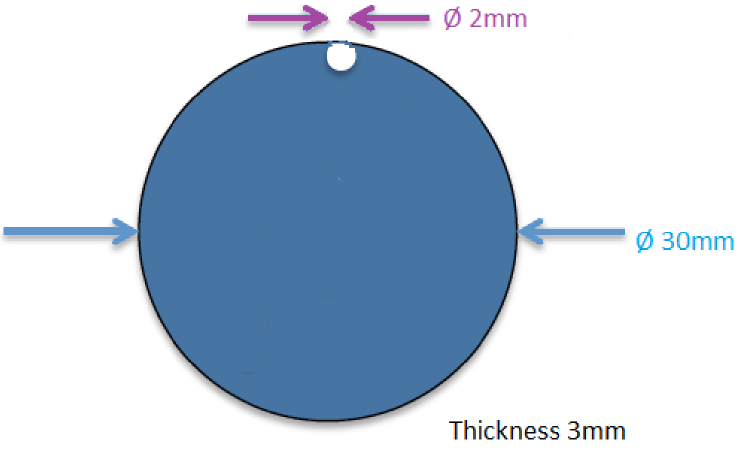


Figure 8 Sample geometry

The two different microstructures examined in this project are shown in Figure 9 and Figure 10. The samples with the solution annealed microstructure, as delivered, showed clear grains of Austenite and Ferrite. There are no visible signs of precipitations.

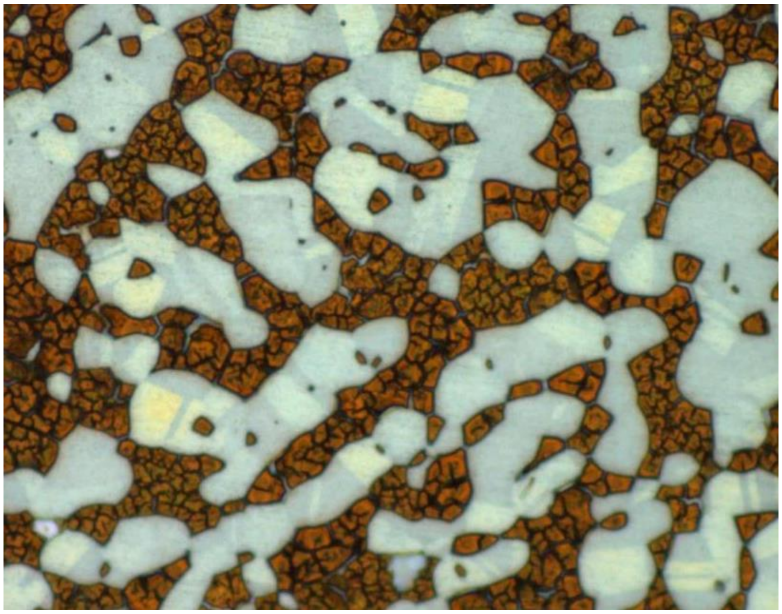


Figure 9 Microstructure of Super Duplex Stainless Steel, Solution Annealed, no sigma phase.

The samples that were heat treated for 7 minutes at 875°C showed precipitations at the grain boundaries. These precipitations are assumed to be mainly σ phase. The volume fraction of precipitations were 5% according to counts done in accordance with ASTM E-562 [23]

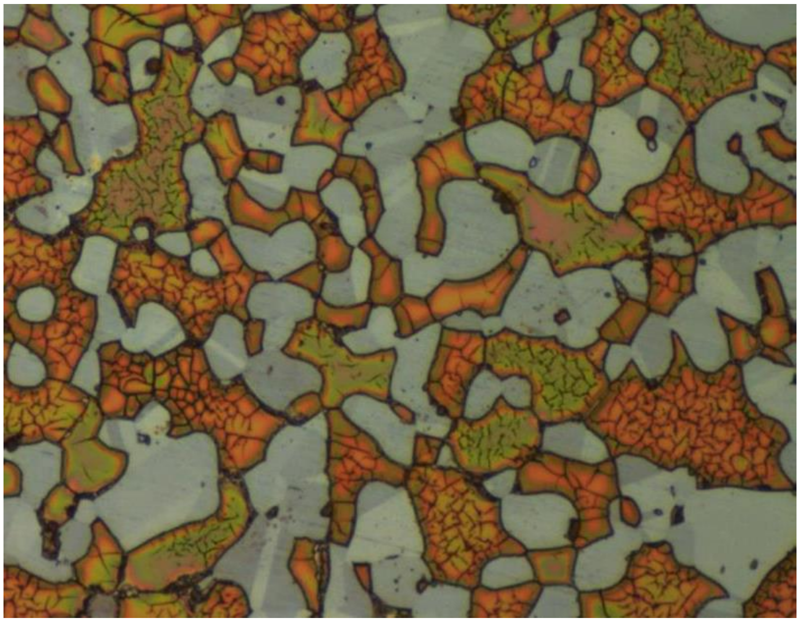


Figure 10 Microstructure of Super Duplex Stainless Steel, Heat treated steel, ~5% sigma phase

A total of 64 samples were tested at temperatures from 25°C to 90°C as shown in table 5. 2 types of microstructures and both pickled and non-pickled surfaces were tested. The count of the precipitates in the heat treated samples gave a volume fraction of 5% (±1,5).

Two samples were tested at each condition for reference. Hence one test contains 2 parallel samples. The results are based on the average value between the two parallel samples. An overview of the tests is given in Table 5.

Table 5 Test overview

TEMP [°C]	SOLUTION ANNEALED, POLISHED	SOLUTION ANNEALED, PICKLED	5 % SIGMA, POLISHED	5 % SIGMA, PICKLED
25	TEST 1	TEST 9	TEST 17	TEST 25
30	TEST 2	TEST 10	TEST 18	TEST 26
40	TEST 3	TEST 11	TEST 19	TEST 27
50	TEST 4	TEST 12	TEST 20	TEST 28
60	TEST 5	TEST 13	TEST 21	TEST 29
70	TEST 6	TEST 14	TEST 22	TEST 30
80	TEST 7	TEST 15	TEST 23	TEST 31
90	TEST 8	TEST 16	TEST 24	TEST 32

The set-ups for the experiments are shown in Figure 11 and Figure 12. The two setups in Figure 11 are equal. The only difference is the type of heater and container used.

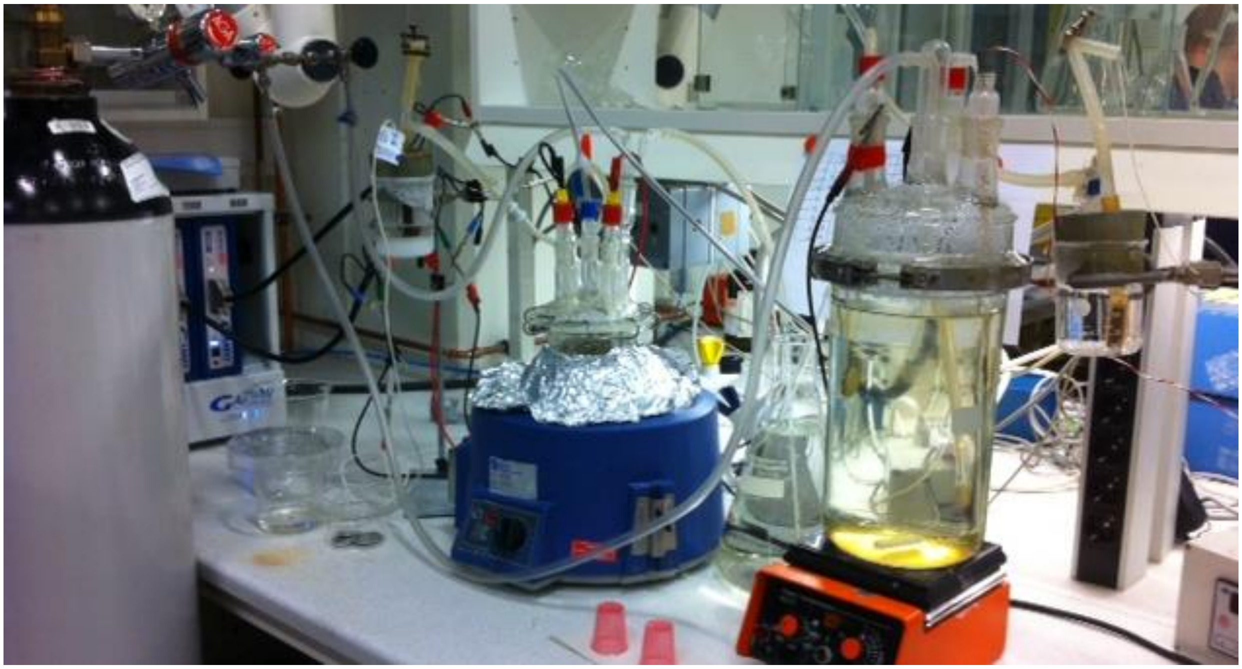


Figure 11 Parallel test set-ups, potentiostat, Nitrogen bottle and logging system.

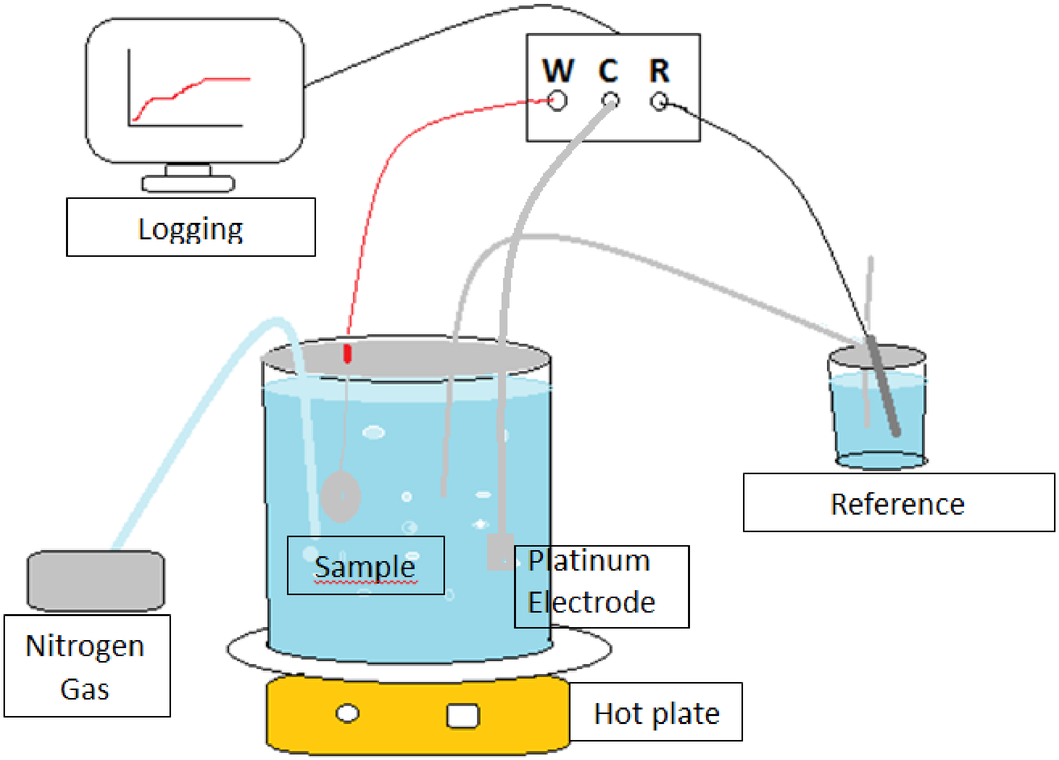


Figure 12 Sketch of test setup
(W – Working electrode, C – Counter Electrode, R – Reference electrode)

2.2 STANDARDS

There are several standards available for pitting corrosion testing and evaluation. The following standards were used in this master thesis.

ASTM G 61 - Standard test method for conducting Cyclic Potentiodynamic Polarization measurement for localized corrosion susceptibility of Iron-, Nickel-, or Cobalt-based alloys [24]

This standard covers a procedure for conducting Cyclic Potentiodynamic Polarization to determine relative susceptibility to localized corrosion in a chloride environment. The solution used is 3,56% Sodium Chloride (by weight). The surface is to be wet polished with 600 grit SiC paper and the sample is to be cleaned in detergent and ultrasonic bath for 5 minutes before it's rinsed in distilled water and dried. The test temperature is 25 ± 1°C. The test cell contains of a container of NaCl solution, a platinum counter electrode, a salt bridge probe connected to a reference electrode and the test specimen. Nitrogen gas is used for purging to remove oxygen for minimum one hour before immersion of the test sample.

ASTM E 562 – Standard Method for determining volume fraction by systematic manual point count [23]

This standard describes a method for calculating volume fraction of constituents using a polished planar cross section of the specimen. The standard includes examples of circular or square grids that can be used. The grid may be in the form of a transparent sheet or it can be superimposed upon the microscope images.

The standard includes formulas to calculate the volume fraction and the statistical precision of the results.

The test grid used in this thesis is shown in Figure 13

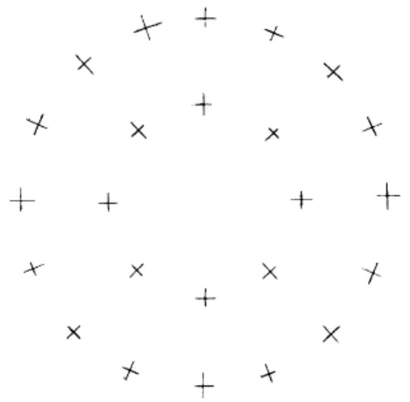


Figure 13 Circular Grid used for determining volume fraction of sigma phase in test specimen.

ASTM A 923-03 Standard test method for detecting Detrimental Intermetallic Phase in Duplex Austenitic/Ferritic Stainless Steels [25]

The standard includes a procedure for electrochemical etching of the surface. The specimen is etched in a 40 % (by weight) sodium hydroxide (NaOH) solution at 1-3V for 5 to 60 seconds. In this thesis 1,5V for 30-40 seconds were used. After etching the specimen are to be rinsed in acetone followed by air drying before it was examined in a confocal microscope. Examples of pictures are given in Figure 8 and Figure9.

ASTM G46-94 Standard Guide for Examination and Evaluation of Pitting Corrosion [26]

This standard describes several techniques for examination and evaluation of pitting corrosion. It includes both destructive and non-destructive methods. A standard rating chart is given to compare the extent of pitting corrosion for different samples. However this method may not be sufficient in itself. In this master thesis this method was used in addition to pit depth measurement using a confocal microscope and visual examination. Pictures of all samples are given in Appendix C.

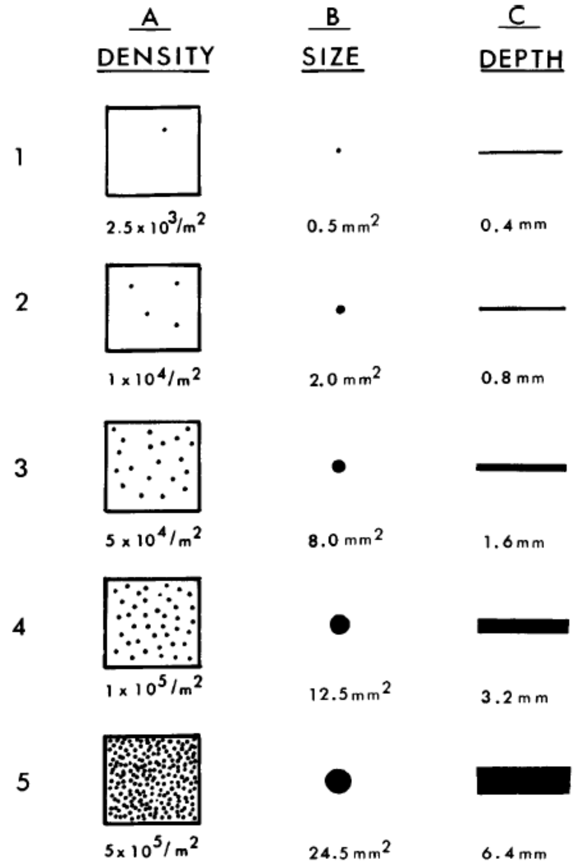


Figure 14 Standard rating charts for pits

NORSOK M-630 [22]

This standard includes material requirement in a collection of Material Data Sheets for a range of different materials used for process equipment and piping. The standard requires a corrosion test according to ASTM G48 and recommends samples pickled for 5 minutes in 20% HNO_3 and 5% HF at 60°C. This pickling method is used in this master thesis.

3 RESULTS

The results from the testing done during this project are described in this chapter. All values for potential refer to a Saturated Calomel Reference Electrode (SCE). The area of the samples used for calculating the current densities was 16,9cm^2. The values given in tables etc. are based on the average of the two values for the parallel samples run at each condition. Where pitting occurred the Pitting Potential is plotted. For the samples showing transpassive behaviour the transpassive potential is plotted.

All values and plots are given in Appendix A. Only a small selection of the results is given in this chapter.

3.1 CYCLIC POLARIZATION SCAN

Cyclic potentiodynamic polarization scans were performed according to the test procedure in section 2.1. The Open Circuit Potential (OCP) from the test start and the measured pH before and after each test are given in Appendix B.

Based on the results of the cyclic polarization scans Pitting potential E_P, Repassivation potential E_{RP} and the passive current density were determined as described in section 1.3. The critical potentials are given in Table 6 to 9. They form the basis for the critical temperatures given in section 3.2.

Table 6 Critical values for Solution Anealed, polished samples

	Temperature (°C)	**E_P (V vs. SCE)**	**E_{RP} (V vs. SCE)**	**i_{pass} (µA/cm^2)**
Test 1	20	0.965	1.0395	1.52
Test 2	30	0.957	0.971	1.43
Test 3	40	0.905	1.008	1.345
Test 4	50	0.995	0.8475	1.78
Test 5	60	0.967	0.333	1.53
Test 6	70	0.845	0.063	1.92
Test 7	80	0.533	-0.0484	5.835
Test 8	90	0.2075	-0.0125	0.75

Table 7 Critical values for Solution Anealed, pickled samples

	Temperature (°C)	E_p (V vs. SCE)	E_{RP} (V vs. SCE)	i_{pass} (µA/cm^2)
Test 9	20	0.947	1.003	2
Test 10	30	0.9115	0.977	1.515
Test 11	40	0.8705	1.0015	1.85
Test 12	50	0.89	0.94	2.085
Test 13	60	0.801	0.197	1.92
Test 14	70	0.845	0.037	2.025
Test 15	80	0.547	-0.00465	1.783
Test 16	90	0.5205	-0.0308	1.38

Table 8 Critical values for 5% Sigma phase, polished samples

	Temperature (°C)	E_P (V vs. SCE)	E_{RP} (V vs. SCE)	i_{pass} (µA/cm^2)
Test 17	20	0.873	0.928	0.90
Test 18	30	0.875	0.91	0.89
Test 19	40	0.834	0.189	0.51
Test 20	50	0.033	0.042	N/A
Test 21	60	0.0575	-0.028	N/A
Test 22	70	-0.01265	-0.0775	N/A
Test 23	80	-0.017	-0.077	N/A
Test 24	90	-0.072	-0.078	N/A

Table 9 Critical values for 5% Sigma phase, pickled samples

	Temperature (°C)	E_P (V vs. SCE)	E_{RP} (V vs. SCE)	i_{pass} (µA/cm^2)
Test 25	20	0.8235	0.927	1.44
Test 26	30	0.6135	0.838	0.71
Test 27	40	0.835	0.85	1.43
Test 28	50	0.2875	0.085	0.76
Test 29	60	0.2135	-0.03	0.4
Test 30	70	0.0755	-0.07015	0.4
Test 31	80	0.174	-0.086	N/A
Test 32	90	0.0282	-0.1005	0.5

Some examples of the polarization curves are shown in Figure 15 and 16. The rest are found in Appendix A. The plots show that for the solution annealed sample with a pickled surface at 50°C, the E_P and E_{RP} are close as there are no significant hysteresis between the pitting and the repassivation potentials. This is typical for a material in a passive state and that the formation of oxides is rapid under these conditions.

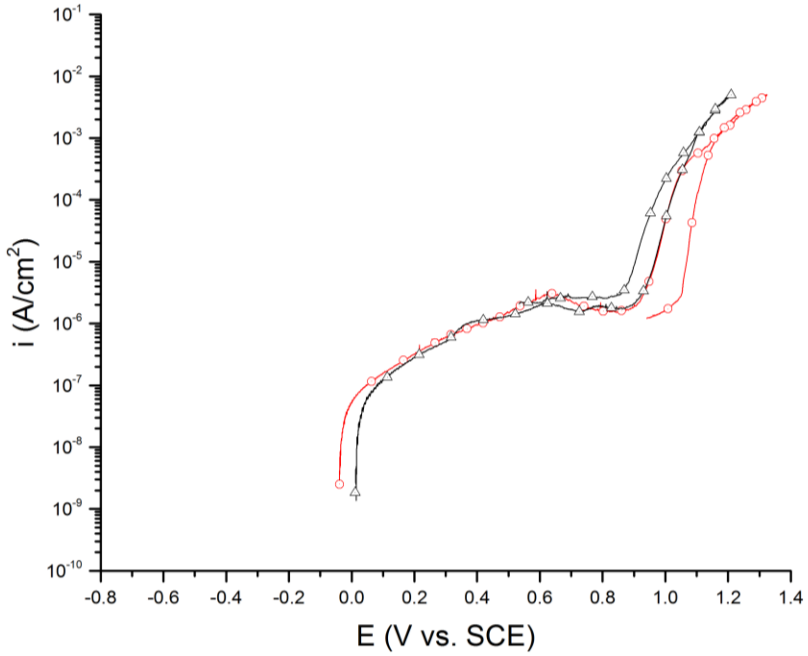


Figure 15 Cylcic polarization scan, Solution Annealed, pickled samples at 50°C

For the equivalent samples run at 80°C there is a large difference between the pitting potentials and the repassivation. This indicates that the sample is corroding and the oxide layer is not stable. It takes a very low potential to repassivate the surface.

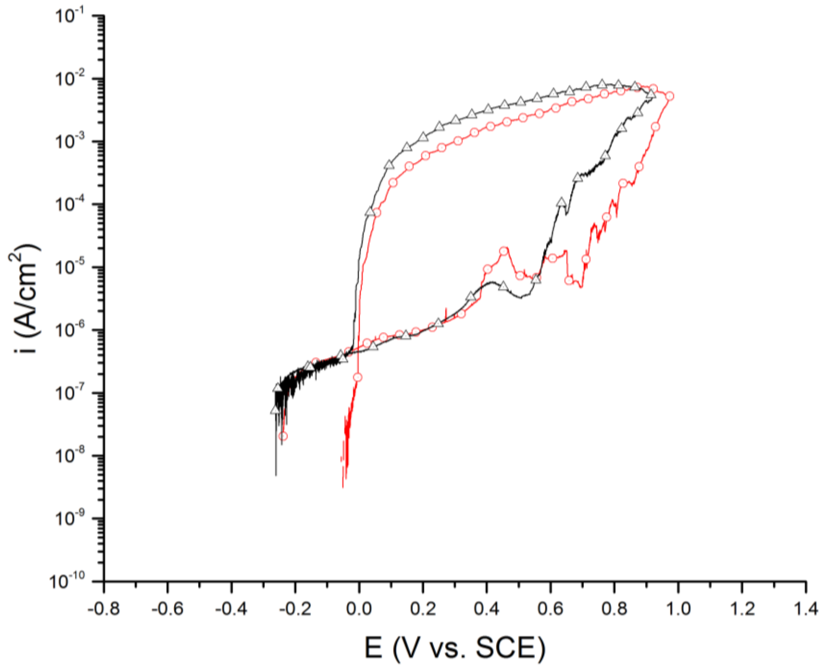


Figure 16 Cylcic polarization scan, Solution Annealed, pickled samples at 80°C

3.2 CRITICAL POTENTIALS AND TEMPERATURES

The critical potentials for the different types of conditions are shown in the plots below. The red circles represent each of the two parallel samples run for each condition. The black circle is the average values.

The Critical Pitting Temperature (CPT) is given where the critical potentials show a sudden drop in Pitting Potential (E_P). The Critical Crevice Temperature (CCT) is given at the drop in Repassivation Potential (E_{RP}). The temperature interval for the tests was 10°C. Hence the accuracy of the CPT and CCT are within the range of ± 9°C.

The critical potentials given in table 6 are plotted in Figure 17 and Figure 18. The solution annealed samples with the as delivered microstructure show a CPT of 65-75°C and a CCT of 55°C as shown in Figure 17 and 18. The plot in Figure 17 E_P vs. Temperature for solution annealed samples with polished surface. Figure 17 shows that the material is resistant against pitting corrosion up to 60°C. Then the pitting potential decreases with increased temperature.

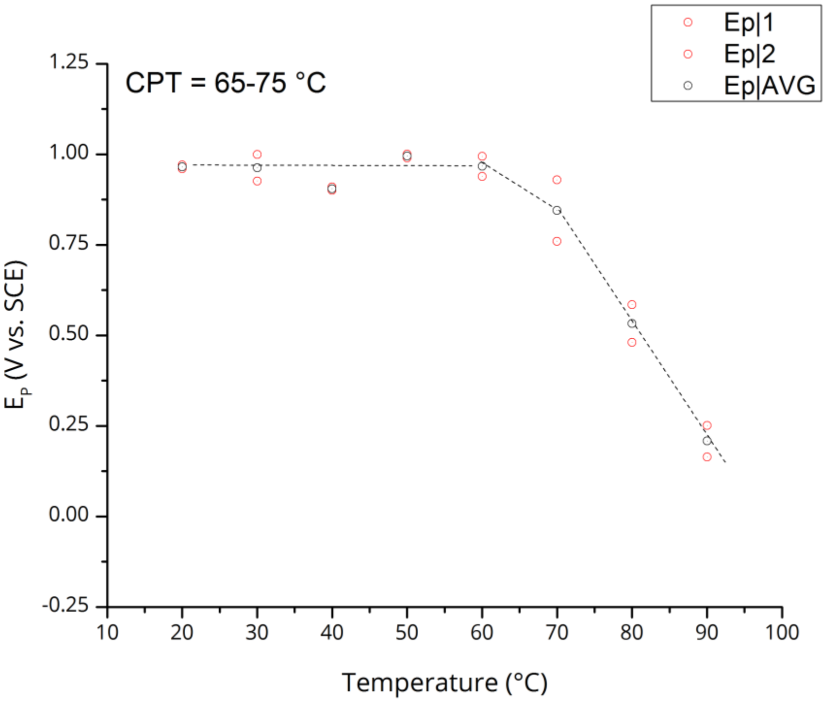


Figure 17 E_P vs. Temperature for solution annealed samples with polished surface.

The repassivation potentials are used to determine the CCT. The results show an even sharper drop than for the pitting potentials and the CCT is estimated to 55°C for the solution annealed, polished condition.

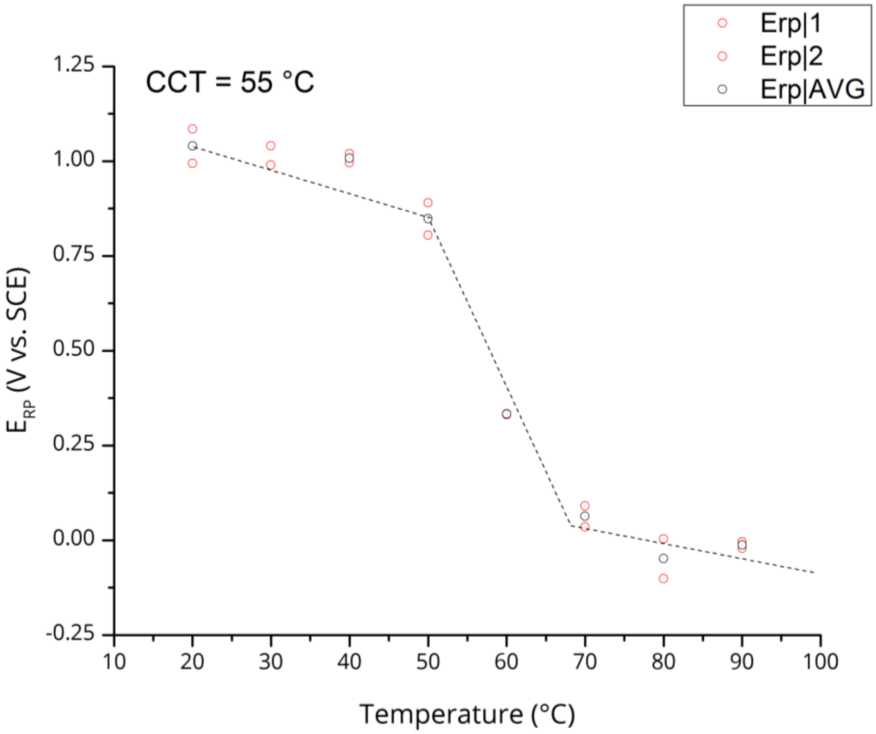


Figure 18 E_{RP} vs. Temperature for solution annealed samples with polished surface

The samples with a pickled surface and the same microstructure from Table 7 show a slightly higher pitting potential at high temperatures as shown in Figure 19 and 20. However the CPT and CCT are 75°C and 55°C respectively as for the polished surface. Pickled surfaces seem to give more repeatable results for the pitting potentials than the non-pickled samples.

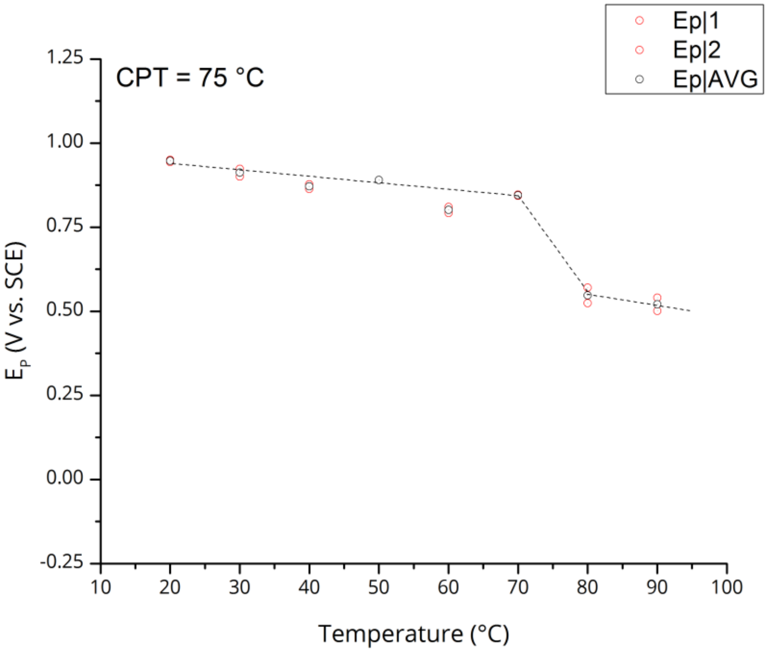


Figure 19 E_P vs. Temperature for solution annealed samples with pickled surface.

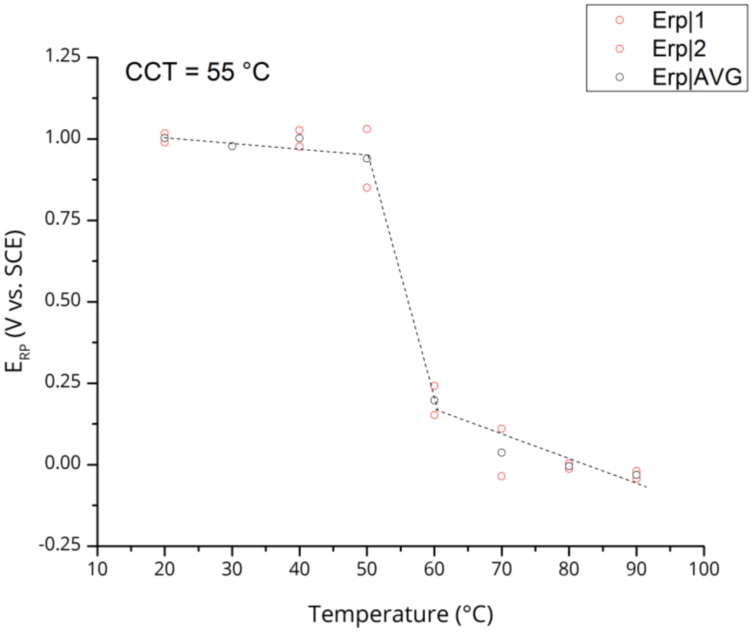


Figure 20 E_{RP} vs. Temperature for solution annealed samples with pickled surface.

The critical temperatures from Table 8 are plotted in Figure 21 and 22. For the heat treated samples with ~5% Sigma phase the critical temperatures are in the range of 35-45°C as shown in Figure 15-18. There are no major differences in the results for the polished or pickled surfaces.

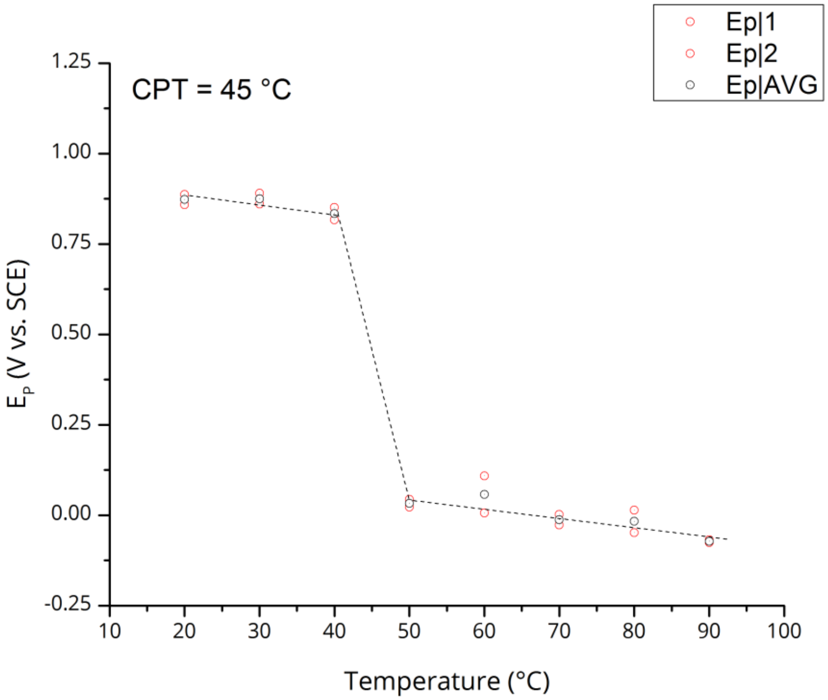


Figure 21 E_P vs. Temperature for 5% Sigma Phase with polished surface

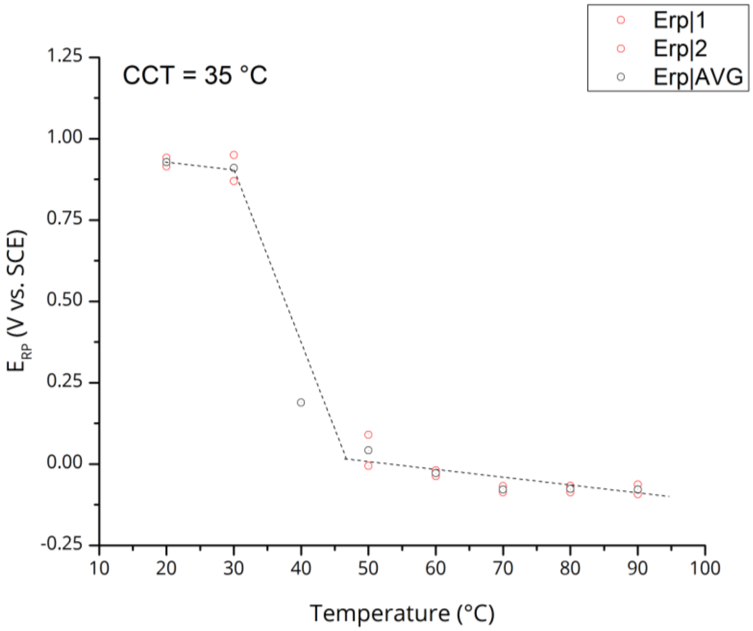


Figure 22 E_{RP} vs. Temperature for 5% Sigma Phase with polished surface

The results from the pickled samples in Table 9 are plotted in Figure 23 and Figure 24. They show a clear drop in potentials at approximately 45°C for both E_P and E_{RP}.

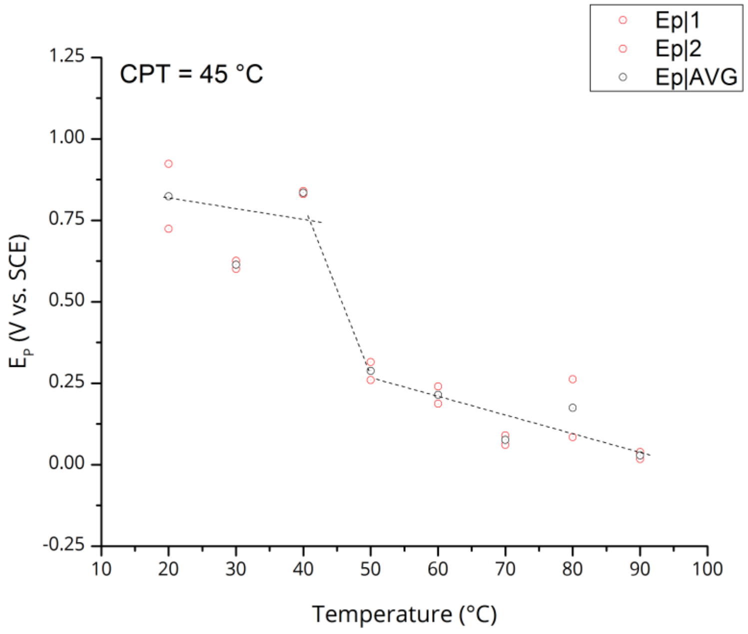


Figure 23 E_P vs. Temperature for 5% Sigma Phase with pickled surface

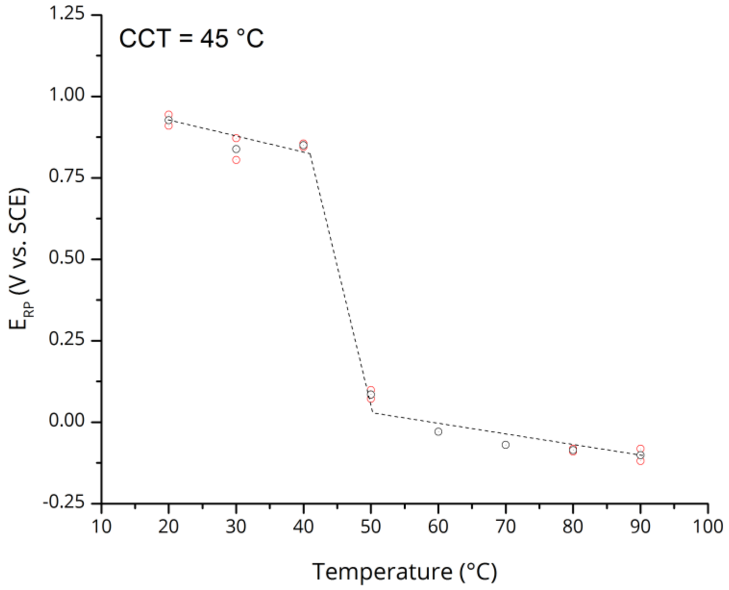


Figure 24 E_{RP} vs. Temperature for 5% Sigma Phase with pickled surface

A summary of critical temperatures found in this master thesis are given in Table 10

Table 10 CPT and CCT for the different conditions tested

MICROSTRUCTURE	SURFACE TREATMENT	CPT	CCT
Solution Annealed	Polished	65-75°C	55°C
Solution Annealed	Pickled	75°C	55°C
5% Sigma Phase	Polished	45°C	35°C
5% Sigma Phase	Pickled	45°C	45°C

3.3 EVALUATION OF SURFACE AFTER TESTING

The surfaces were studied and evaluated after the testing to confirm the presence and extent of pits on the corroded surfaces. Samples were studied in a confocal microscope. These results are shown in Figure 25 to 28. The pictures are taken with a magnification of 2,5x. To reveal pits, the oxides were removed by polishing the sample with 3µm diamond suspension. This was done to make sure that the dark spots were pits and not just surface contamination. For the solution annealed samples small scattered pits were found at 50°C. The oxide layer was discoloured.

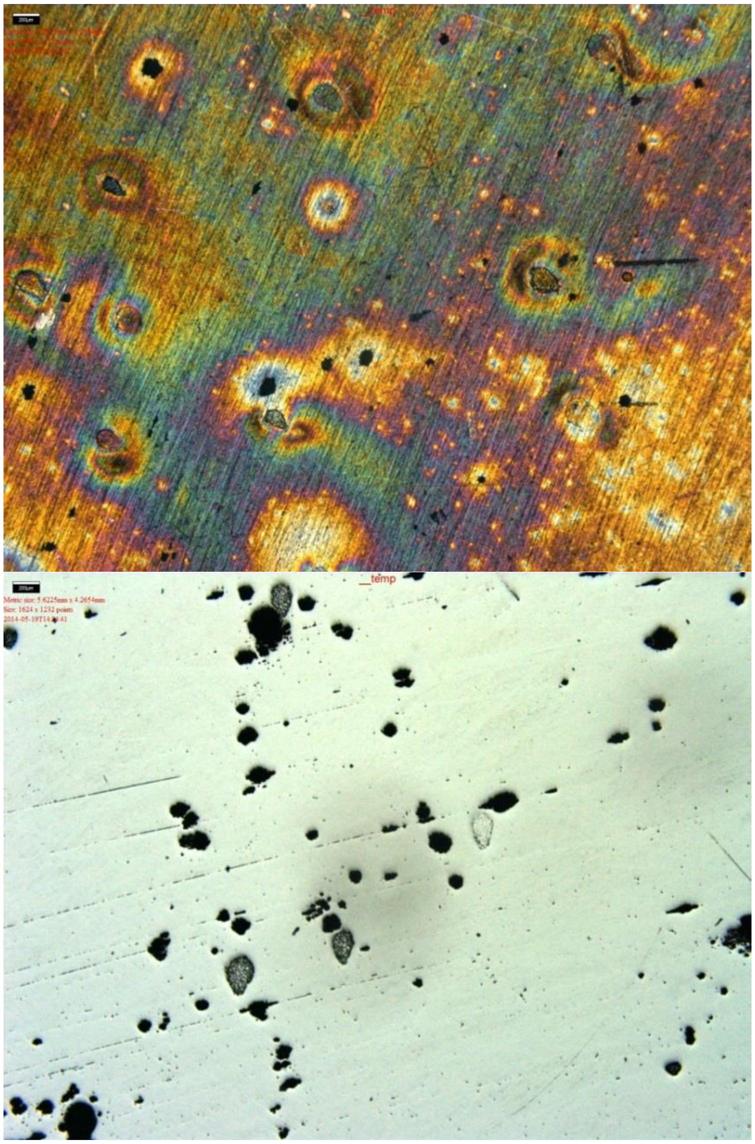


Figure 25 Test 12: Solution Anealed, pickled surface, 50°C, magnification 2,5x, Top: Surface with oxides, Bottom: Diamond polished surface.

At 60°C larger and deeper pits were detected. The oxide layer had also changed its colour.

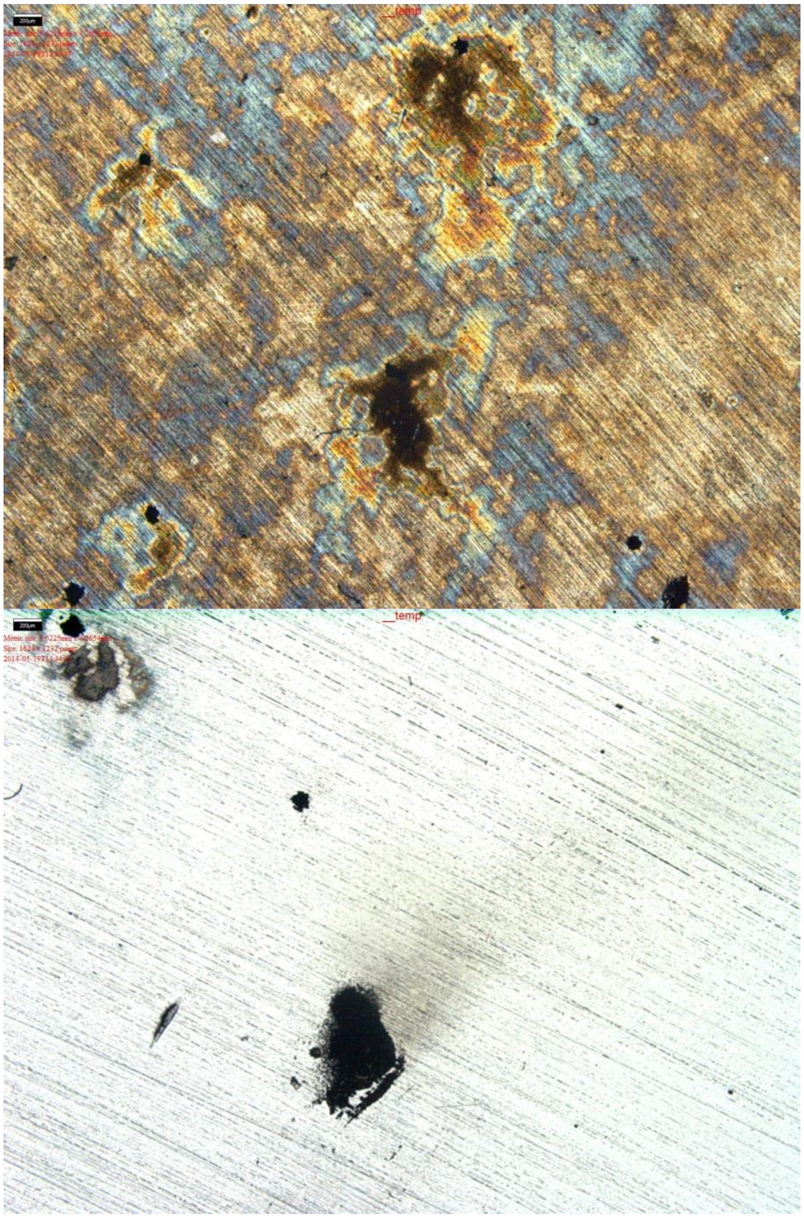


Figure 26 Test 13: Solution Anealed, pickled surface, 60°C, magnification 2,5x, Top: Surface with oxides, Bottom: Diamond polished surface.

The samples containing sigma phase precipitates the critical temperature limits are lower. Some of the samples showed no passive behaviour either and the corrosion had a more uniform dominance and not so clear pitting corrosion behaviour. The pitting corrosion attacks seem to have been concentrated more on the edges of the samples rather than on the polished surface. Figure 27 and 28 show the microstructure images of 2 samples with 5% sigma phase after testing. The pits are smaller than and not as distinct as for the solution annealed samples. They seem to be less deep, but the true depth and size was not measured.

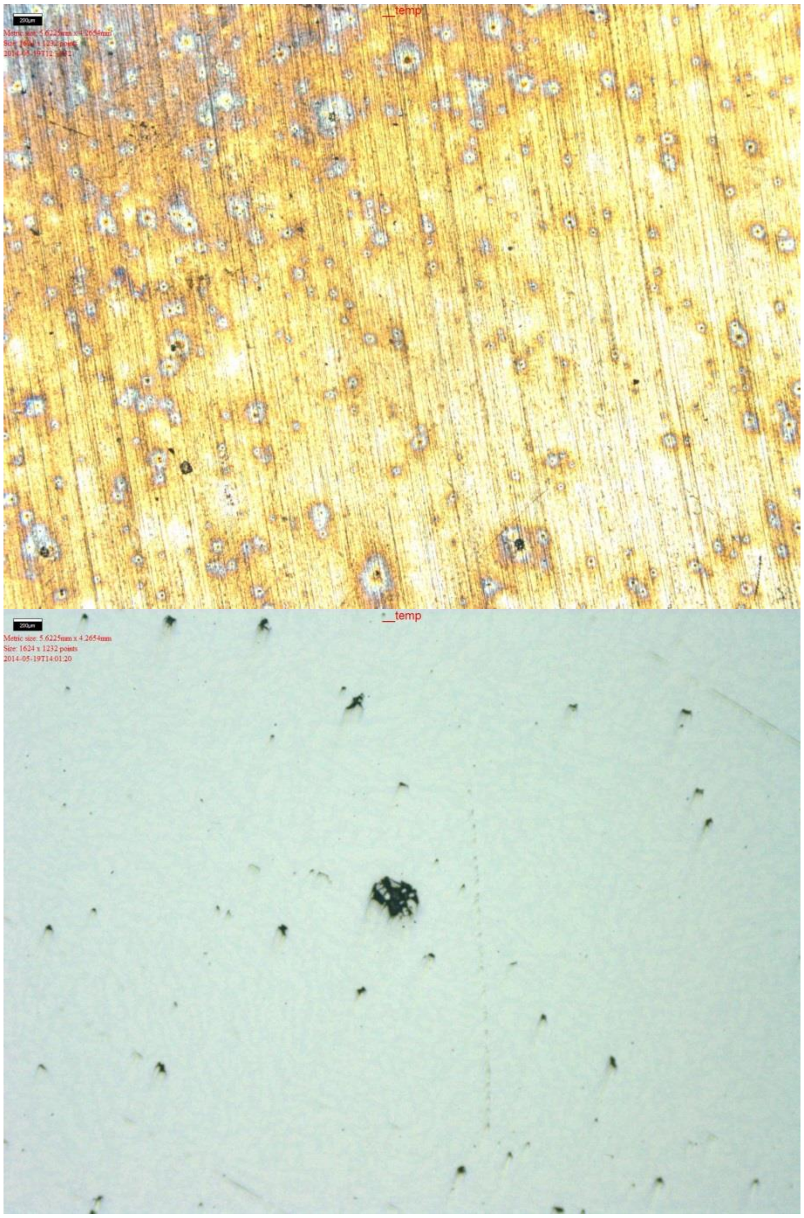


Figure 27 Test 27: 5% sigma phase, pickled surface, 40°C, magnification 2,5x
Top: with oxides, Bottom: Diamond polished surface.

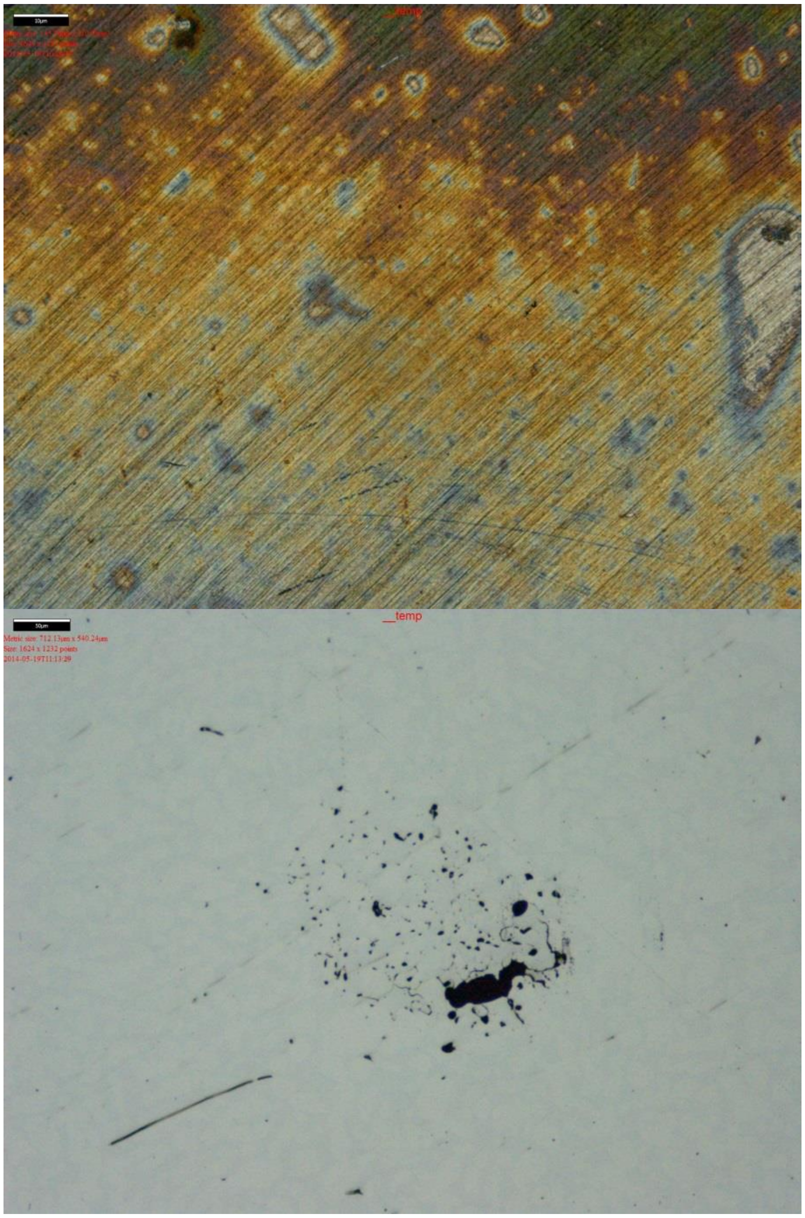


Figure 28 Test 28: 5% sigma phase, pickled surface, 50°C, magnification 2,5x
Top: with oxides, Bottom: Diamond polished surface.

4 DISCUSSION

Most of the results found in this project are according to what was expected based on previous research with some deviations. In this chapter the most interesting results from this project are discussed.

4.1 CORROSION POTENTIALS

From the plots from the cyclic polarization scans found in Appendix A it is shown that the test gives reproducible results as there are no large deviations between the two samples run in parallel. The deviations are smaller for the pickled samples than the grinded samples. This is probably due to a cleaner and more homogenous surface for the pickled samples.

The corrosion potentials for Super Duplex Stainless Steel are strongly dependent on temperature. Both the pitting and repassivation potentials show a significant change between 50 and 60°C for the solution annealed samples. The tests performed in this master thesis show a difference between the pitting potential and the repassivation potential ($E_P - E_{RP}$) changes from ≈150mV to ≈600mV over the 10° temperature difference. This indicates that the immunity of the material to localized corrosion is reduced.

The current densities show that the solution annealed samples show a clearly passive behaviour and the passive current density is in the range of 1,5-2 $\mu A/cm^2$. For the heat treated samples containing sigma precipitates this value is lower (range of 0,5-0,7$\mu A/cm^2$) and for many of the samples there is no clear passive current density since the sample is in an active state where the corrosion attacks are more general than localized.

4.2 CRITICAL CORROSION TEMPERATURES

Defining a critical pitting or crevice corrosion temperature for a material is not easy. Many scientists have tried and they all show different results. It's clear that the electrolyte and test method will influence the results. From the literature that was studied in this master thesis CPT values for Super Duplex SS vary from 65 to 95°C. The results from the experiments done in this thesis show that the CPT for as delivered Super Duplex SS in 3,5% NaCl solution is close to 70±5°C.

If the microstructure is destroyed by poor heat treatment, welding or other treatments causing precipitation of sigma phase, the resistance against corrosion is drastically reduced. The CPT for Super Duplex SS with 5% sigma phase is found to be between 40 and 50°C. The presence of sigma phase should therefore be discovered in a corrosion test like the commonly used ASTM G84 test. It also documents that the use of PRE number in itself is not enough to evaluate the resistance against localized corrosion. All samples used in this project had the same chemical composition and with that the same PREN, but not the same pitting resistance.

Some of the same trends are found for crevice corrosion; however the drop in critical temperature CCT is not as large as for pitting corrosion. The CCT for as delivered, solution annealed material is found to be 55°C as for material with precipitates the CCT is closer to 40±5°C. The available literature gives values for CCT of 35-60°C but for crevice corrosion, the test method and sample preparation will make a large impact. This makes it difficult to compare the values.

In this project two types of surface treatment were evaluated. The results show no greater effect of the pickling except slightly more reproducible results. Some of the noise was also eliminated. This is most likely due to a cleaner surface and less contamination on the surface. Some of the oxide residuals on the sample edges were also removed by the pickling process.

4.3 SOURCES OF ERROR

The potentiostat was very sensitive to noise especially at low current densities. The producers of the potentiostat Gamry were contacted and some adjustments were made, but the noise had to be removed after testing.

The cells contained approximately 5 litres of electrolyte. It took a long time to heat the electrolyte to the correct temperature. Some variation in temperature at the top and bottom of the cell was inevitable. A smaller cell is recommended for similar experiments.

The pH meter was broken for some time before it was discovered. Some of the pH values may be wrong. However the values seemed to be in the range of pH 6 to 8 with little change before and after the tests.

The pickling process did not seem to remove all oxides on the sides of the samples. The front and back of the samples were polished, but some residual oxides were observed even after pickling. Square samples would be recommended to make polishing or polishing of the sides would be easier that on a round sample. Some samples showed large pits on the edges and a lot less attack on the polished surfaces. This may have affected the results.

The microscopy images are taken with a certain magnification, however when this master thesis is printed, the document is scaled to fit the right format. This magnification will therefore not be correct, but it will be ok for comparing the different images at the same magnification.

4.4 FURTHER WORK

To find out more about Super Duplex SS in chloride environments more tests could be done. It could be interesting to focus on the temperatures around the critical temperatures (30-70°C) and to test specimen with different volume fractions of sigma phase, e.g. 1% sigma phase. To test samples with different amount of precipitates would give valuable information about how much sigma phase can be detected by corrosion testing and how the amount of precipitates will affect the corrosion properties of the material.

5 CONCLUSION

A study of available literature and a series of tests have been performed to investigate how the presence of secondary phases and different surface finish affect the corrosion properties of Super Duplex Stainless Steel in a chloride environment.

The experiments show that Super Duplex Stainless Steel has a Critical Pitting Temperature between 65°C and 75°C. If sigma phase precipitates are present the Critical Pitting Temperature is lowered to 55°C.

The critical crevice corrosion temperature changes from 55°C for a solution annealed material to approximately 40°C for material with sigma phase precipitation.

Pickled surfaces give more repeatable results and less noise on the results indicating that a cleaner surface is preferred.

Pitting corrosion tests according to the executed procedure can be used to detect material with poor heat treatment and precipitation of sigma phase.

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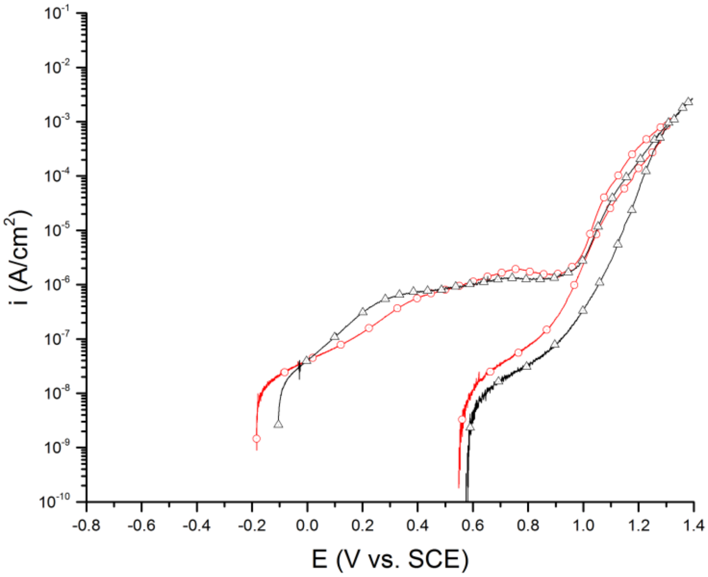
APPENDIX A POTENTIODYNAMIC TEST RESULTS

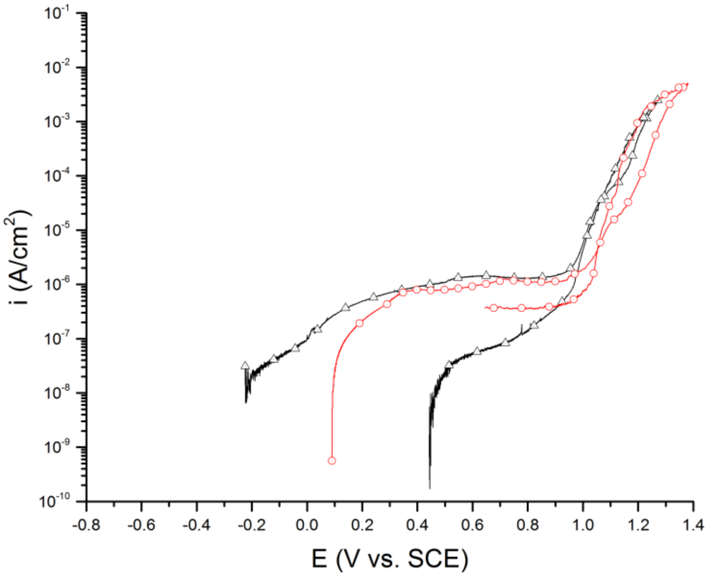
Results for Solution Annealed, polished samples:

Table 11 Critical values for Solution Anealed, polished samples

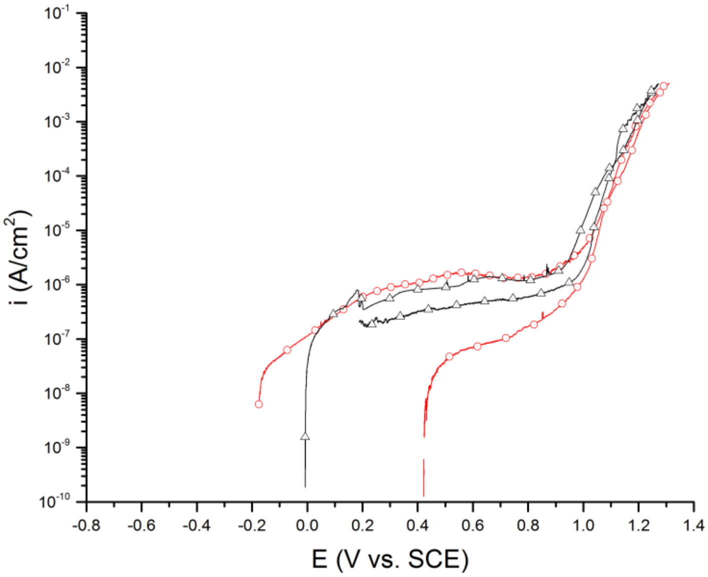
	TEMPERATURE (°C)	EP (V VS. SCE)	ERP (V VS. SCE)	IPASS (µA/CM2)
TEST 1	20	0.965	1.0395	1.52
TEST 2	30	0.957	0.971	1.43
TEST 3	40	0.905	1.008	1.345
TEST 4	50	0.995	0.8475	1.78
TEST 5	60	0.967	0.333	1.53
TEST 6	70	0.845	0.063	1.92
TEST 7	80	0.533	-0.0484	5.835
TEST 8	90	0.2075	-0.0125	0.75



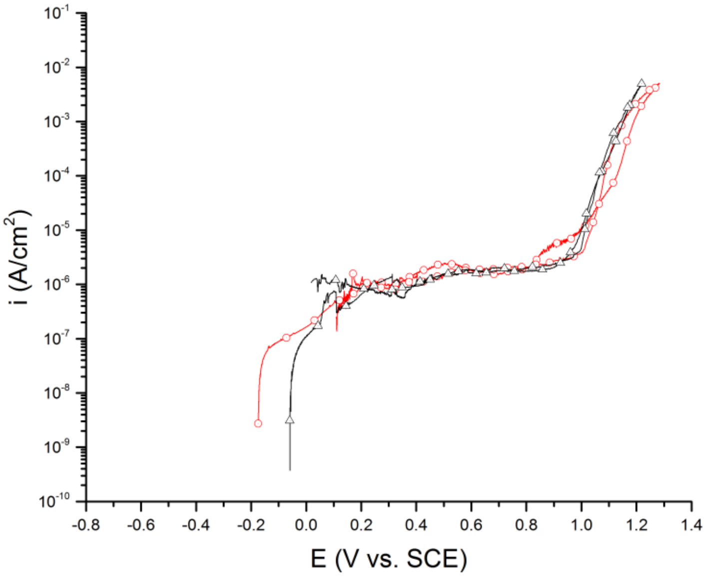
Plot TEST 1



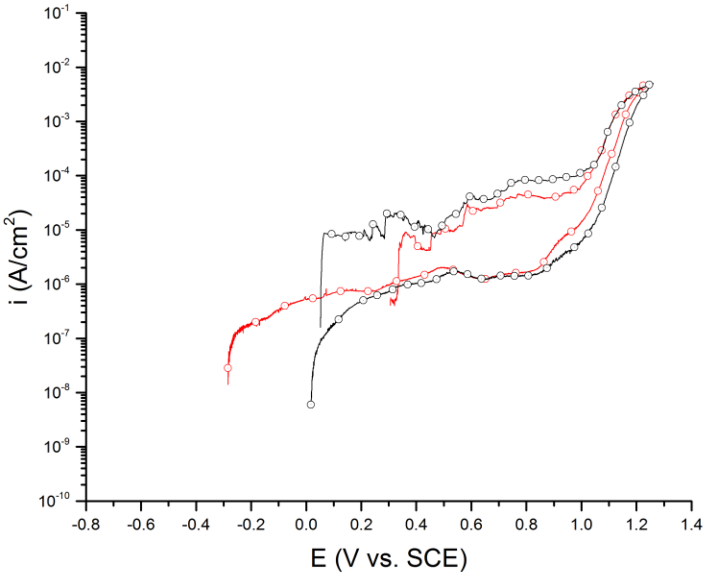
Plot TEST 2



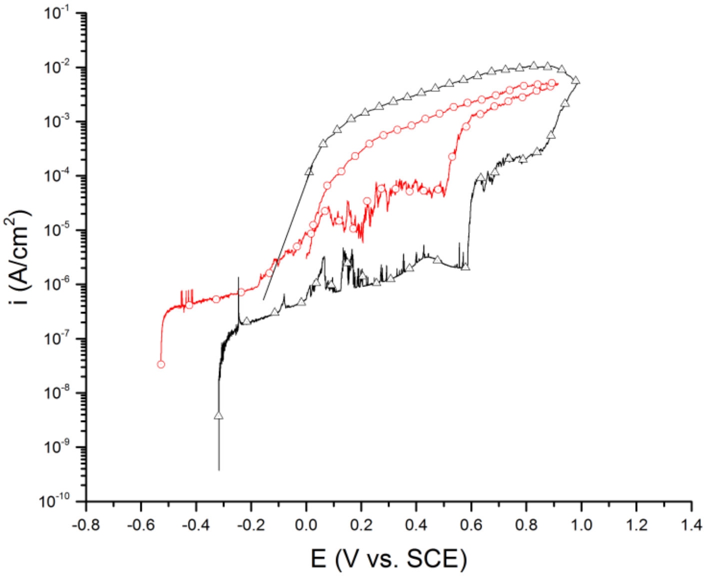
Plot TEST 3



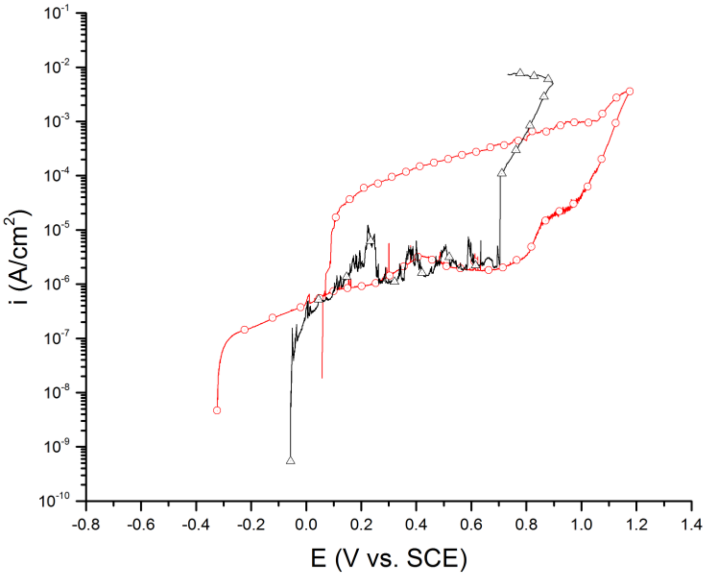
Plot TEST 4



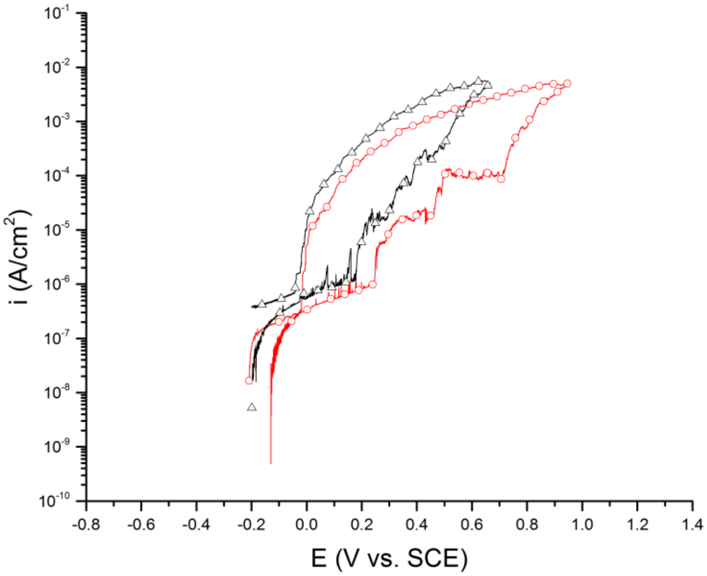
Plot TEST 5



Plot TEST 6



Plot TEST 7

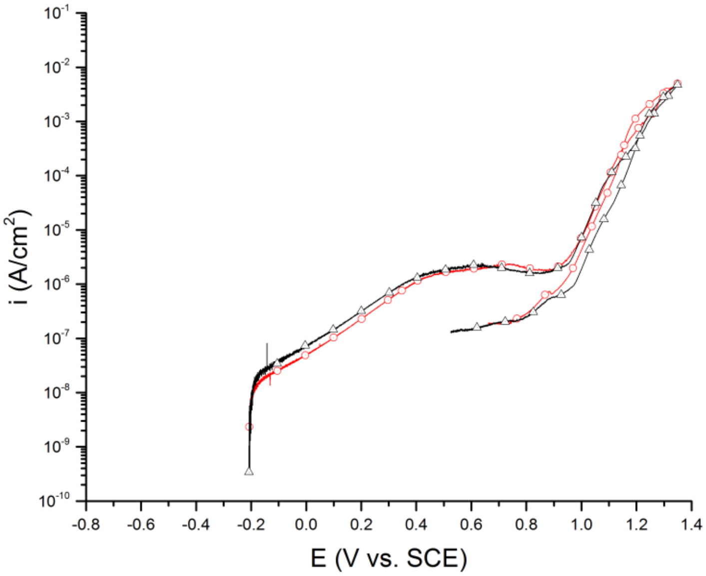


Plot TEST 8

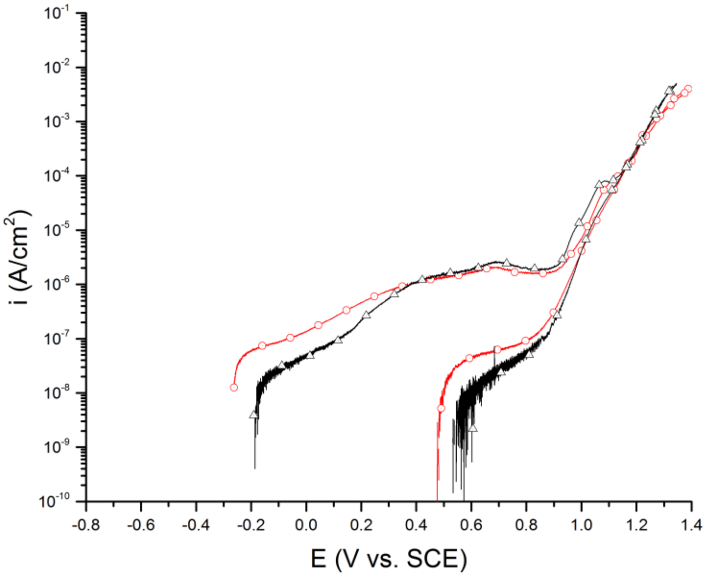
Results for Solution Annealed, Pickled Samples:

Table 12 Critical values for Solution Anealed, pickled samples

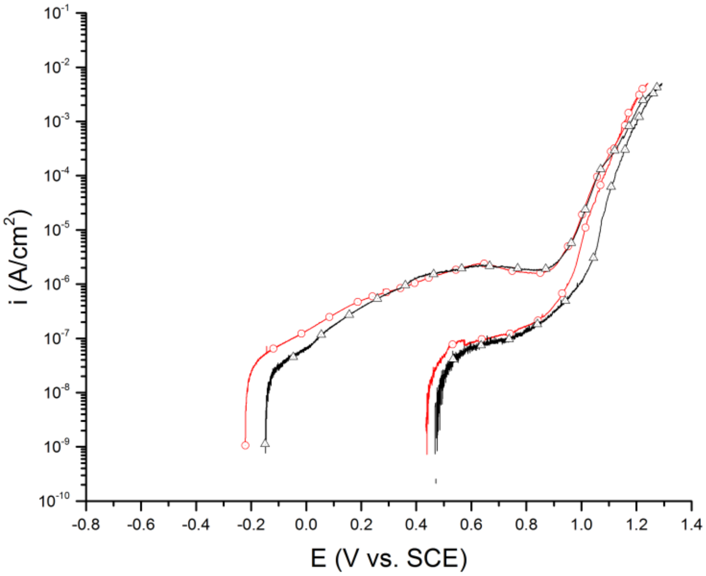
	TEMPERATURE (°C)	EP (V VS. SCE)	ERP (V VS. SCE)	IPASS (µA/CM2)
TEST 9	20	0.947	1.003	2
TEST 10	30	0.9115	0.977	1.515
TEST 11	40	0.8705	1.0015	1.85
TEST 12	50	0.89	0.94	2.085
TEST 13	60	0.801	0.197	1.92
TEST 14	70	0.845	0.037	2.025
TEST 15	80	0.547	-0.00465	1.783
TEST 16	90	0.5205	-0.0308	1.38



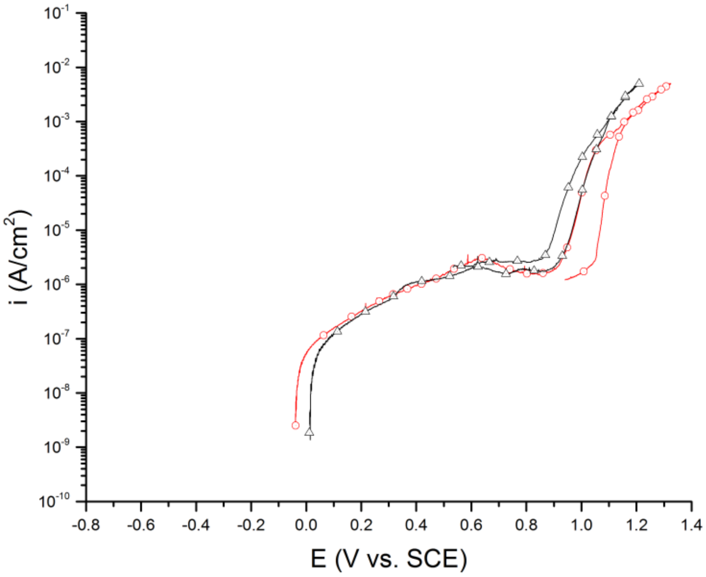
Plot TEST 9



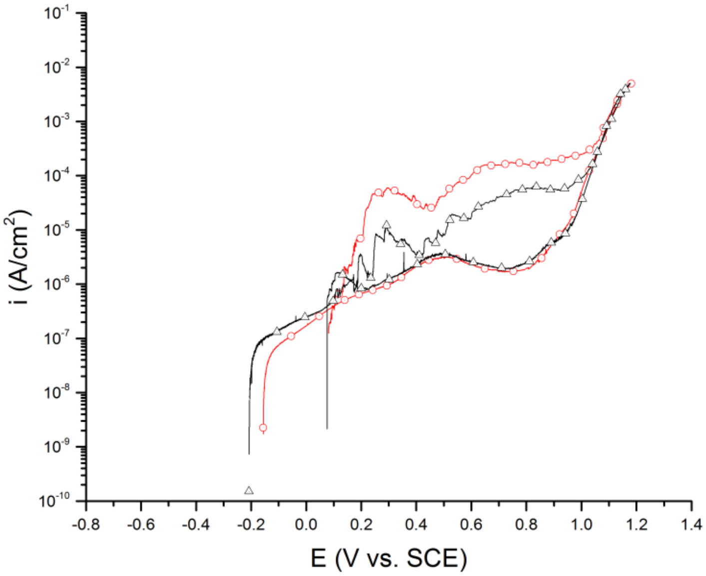
Plot TEST 10



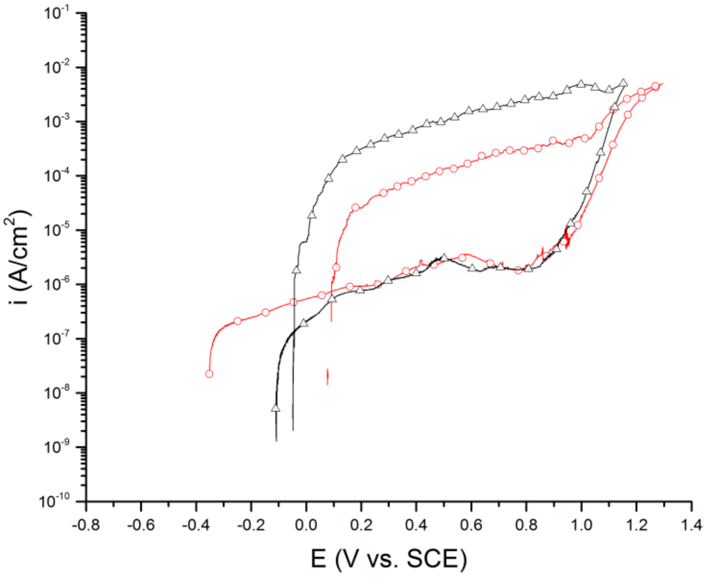
Plot TEST 11



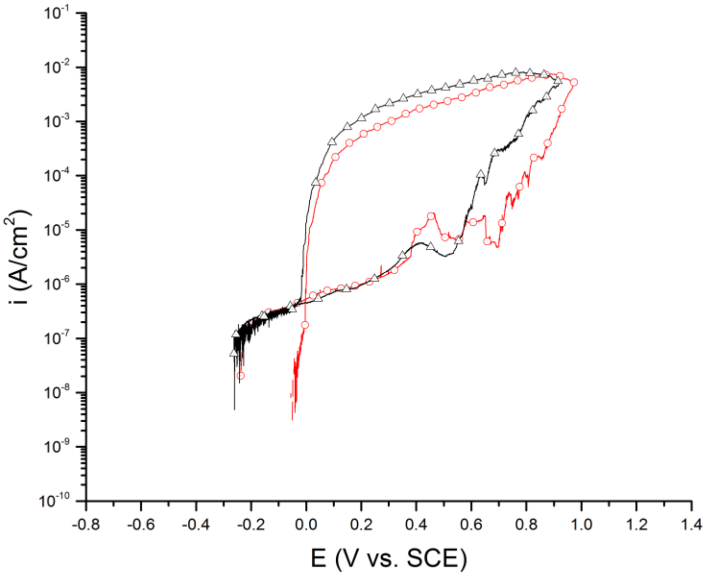
Plot TEST 12



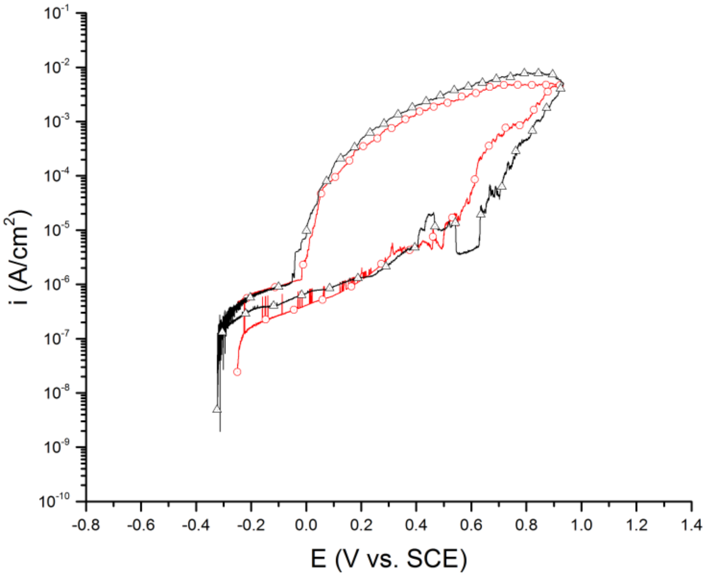
Plot TEST 13



Plot TEST 14



Plot TEST 15

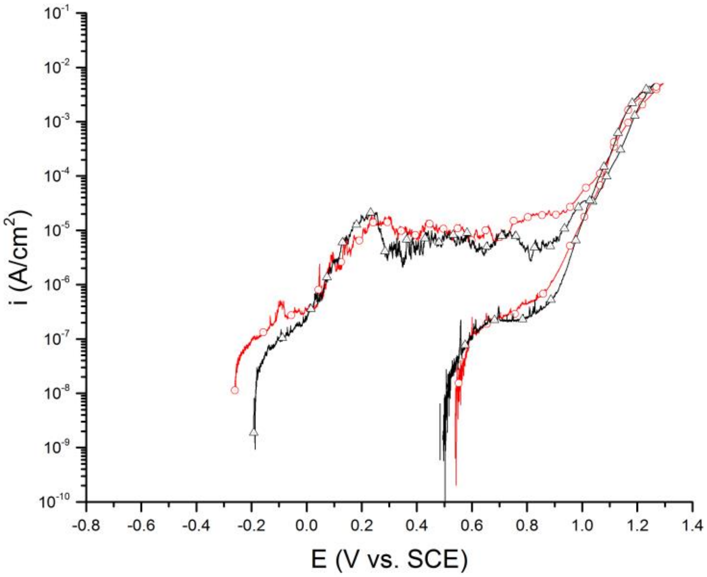


Plot TEST 16

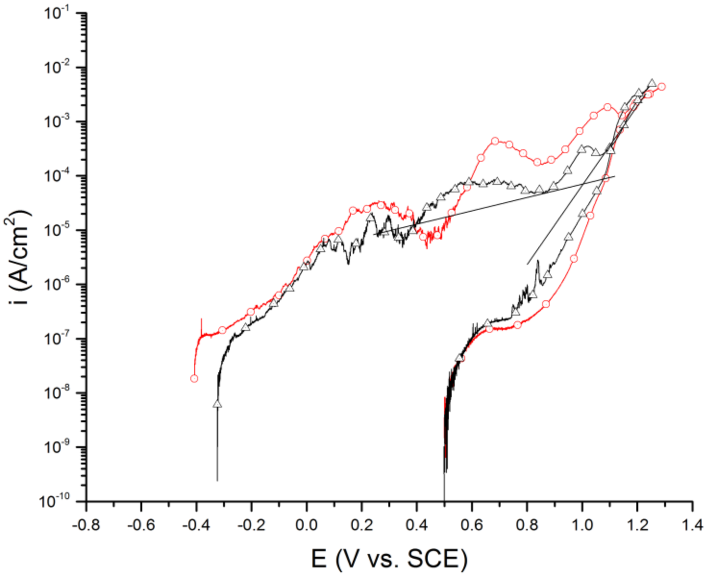
Results for Polished Samples with 5% Sigma Phase:

Table 13 Critical values for 5% Sigma phase, polished samples

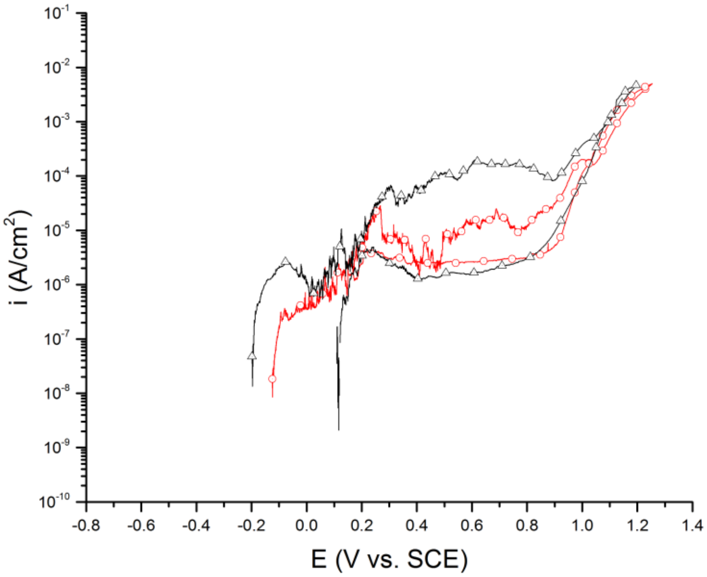
	TEMPERATURE (°C)	EP (V VS. SCE)	ERP (V VS. SCE)	IPASS (μA/CM2)
TEST 17	20	0.873	0.928	0.90
TEST 18	30	0.875	0.91	0.89
TEST 19	40	0.834	0.189	0.51
TEST 20	50	0.033	0.042	N/A
TEST 21	60	0.0575	-0.028	N/A
TEST 22	70	-0.01265	-0.0775	N/A
TEST 23	80	-0.017	-0.077	N/A
TEST 24	90	-0.072	-0.078	N/A



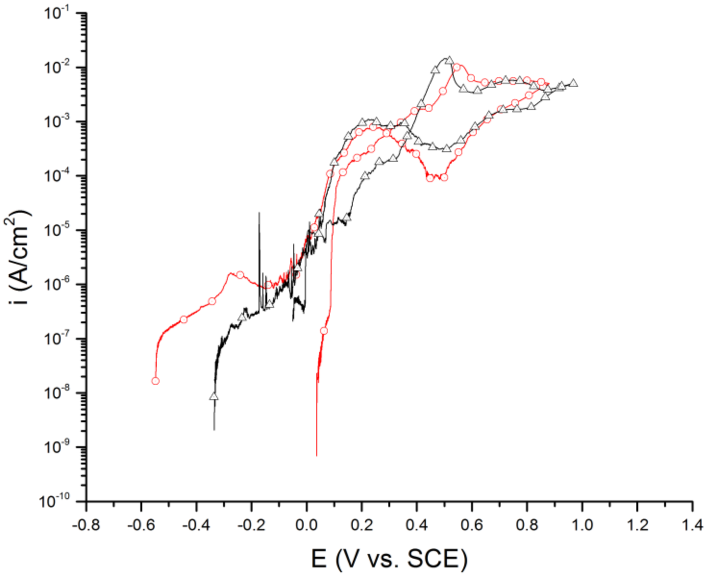
Plot TEST 17



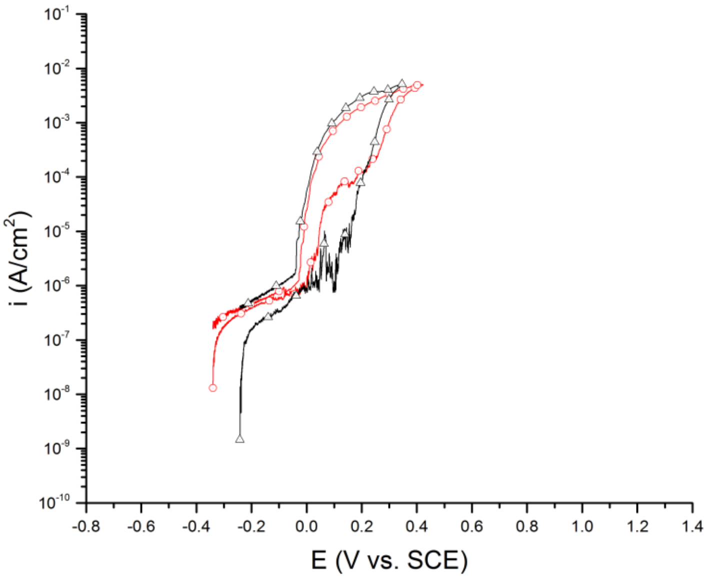
Plot TEST 18



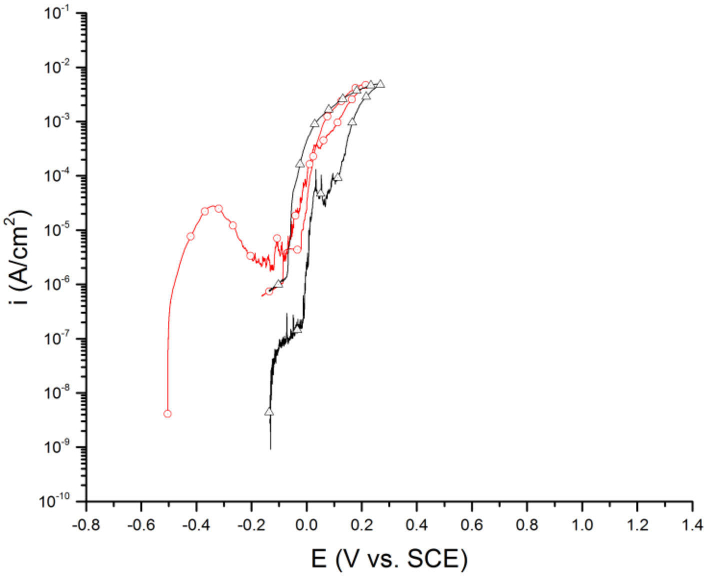
Plot TEST 19



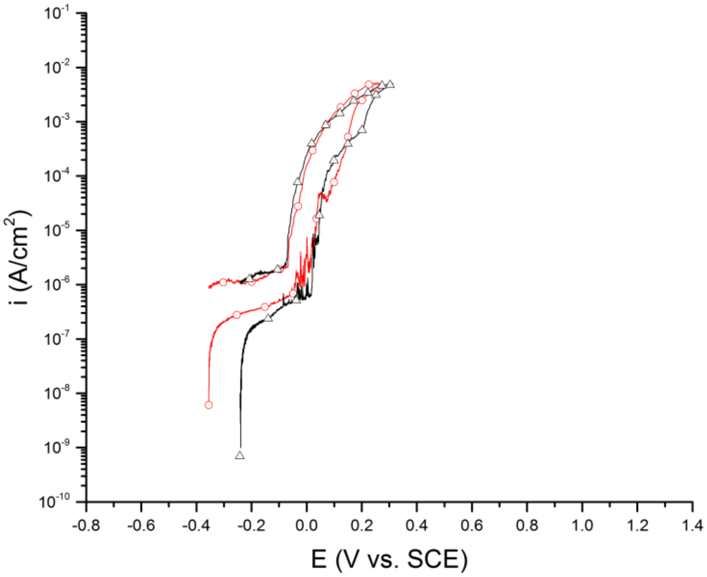
Plot TEST 20



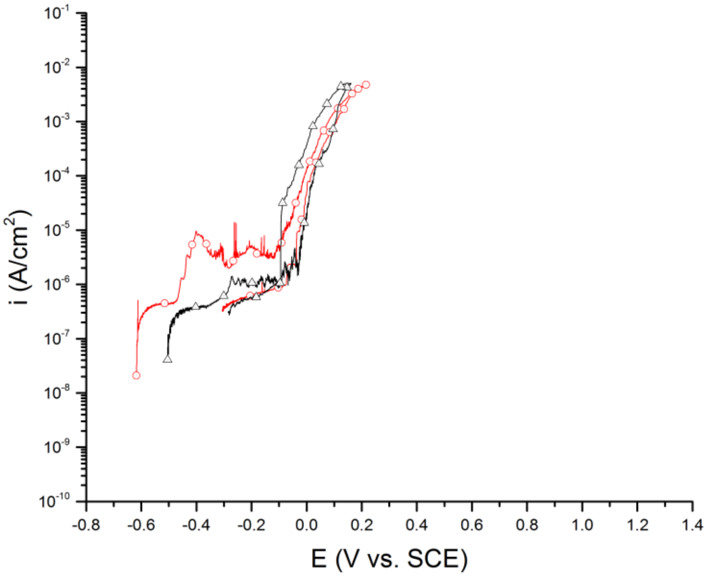
Plot TEST 21



Plot TEST 22



Plot TEST 23

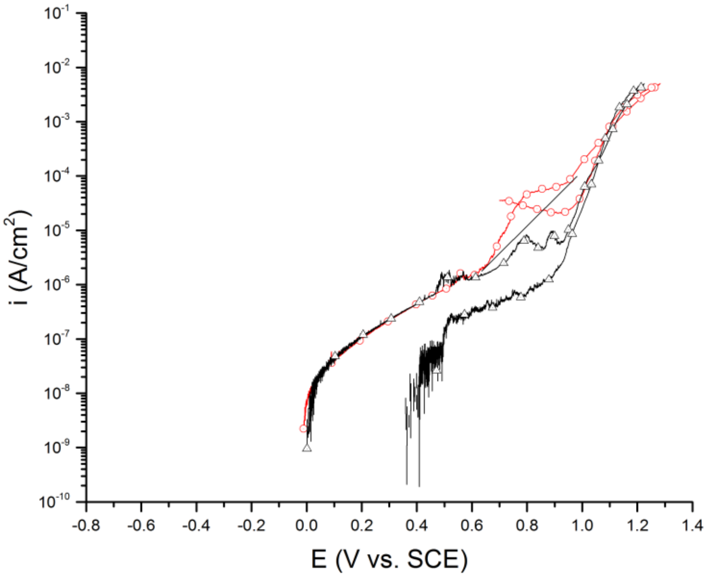


Plot TEST 24

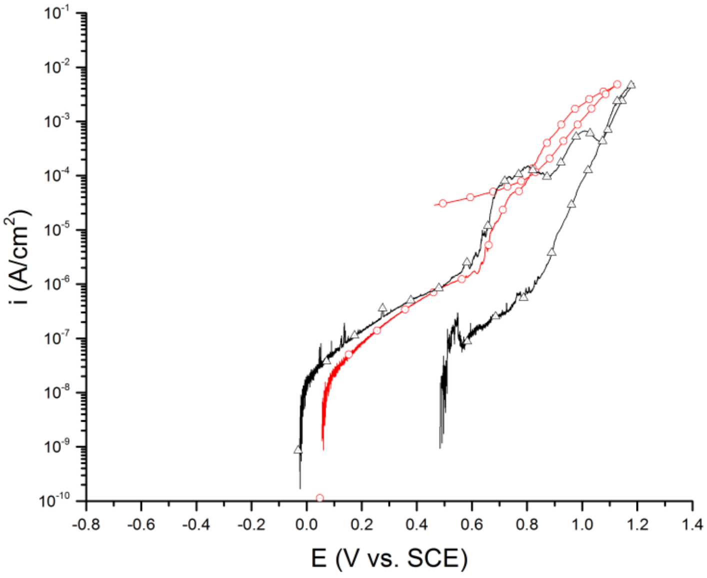
Results for Pickled Samples with 5% Sigma Phase:

Table 14 Critical values for 5% Sigma phase, pickled samples

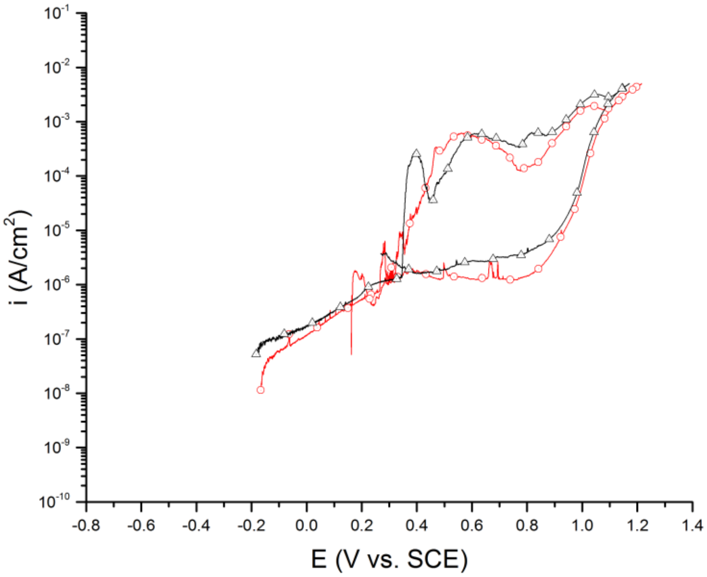
	TEMPERATURE (°C)	EP (V VS. SCE)	ERP (V VS. SCE)	IPASS (µA/CM2)
TEST 25	20	0.8235	0.927	1.44
TEST 26	30	0.6135	0.838	0.71
TEST 27	40	0.835	0.85	1.43
TEST 28	50	0.2875	0.085	0.76
TEST 29	60	0.2135	-0.03	0.4
TEST 30	70	0.0755	-0.07015	0.4
TEST 31	80	0.174	-0.086	N/A
TEST 32	90	0.0282	-0.1005	0.5



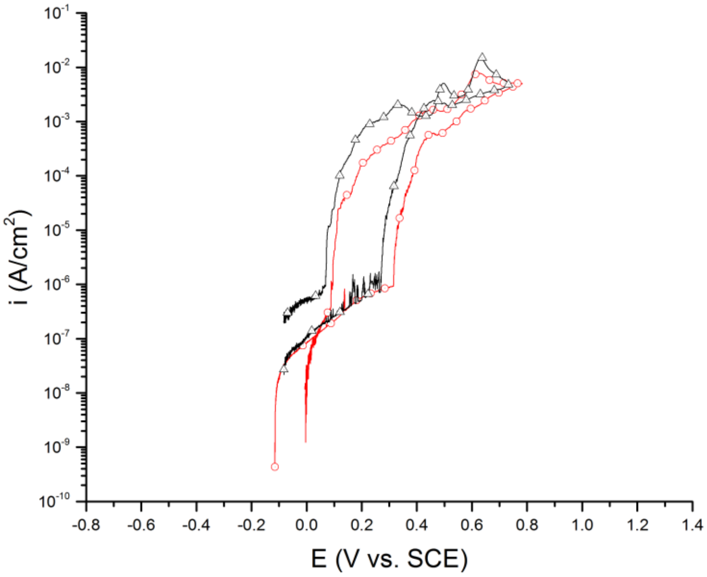
Plot TEST 25



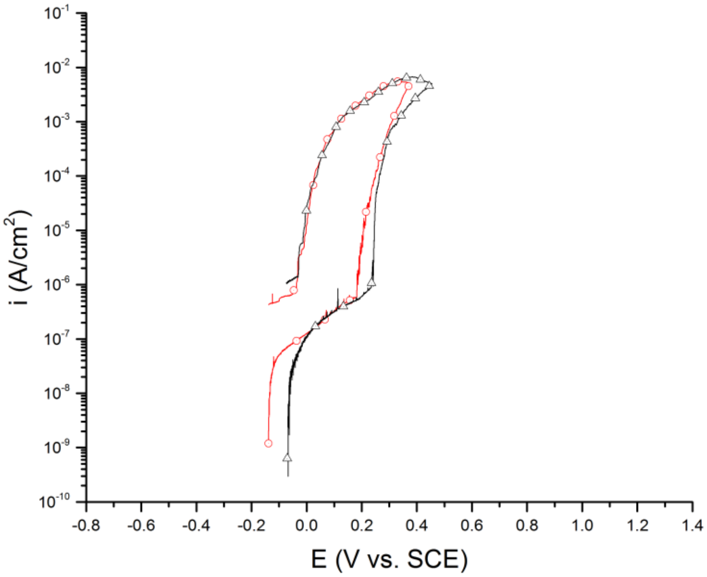
Plot TEST 26



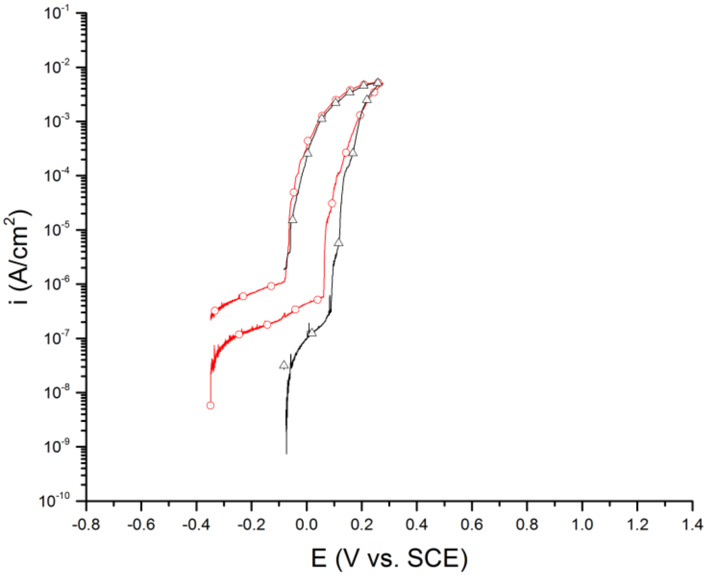
Plot TEST 27



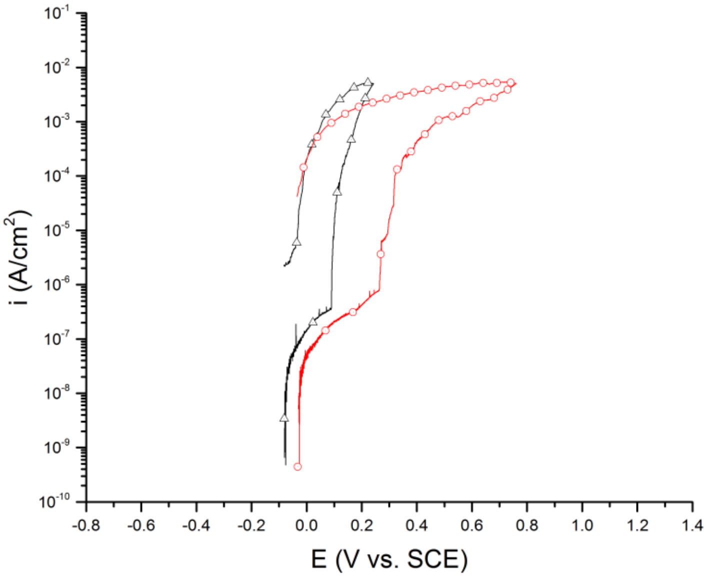
Plot TEST 28



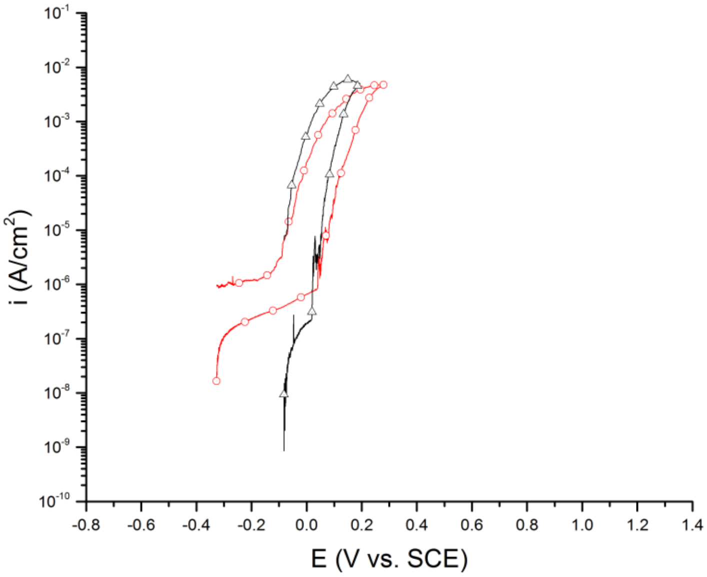
Plot TEST 29



Plot TEST 30



Plot TEST 31



Plot TEST 32

APPENDIX B OPEN CIRCUIT POTENTIALS AND MEASURED PH

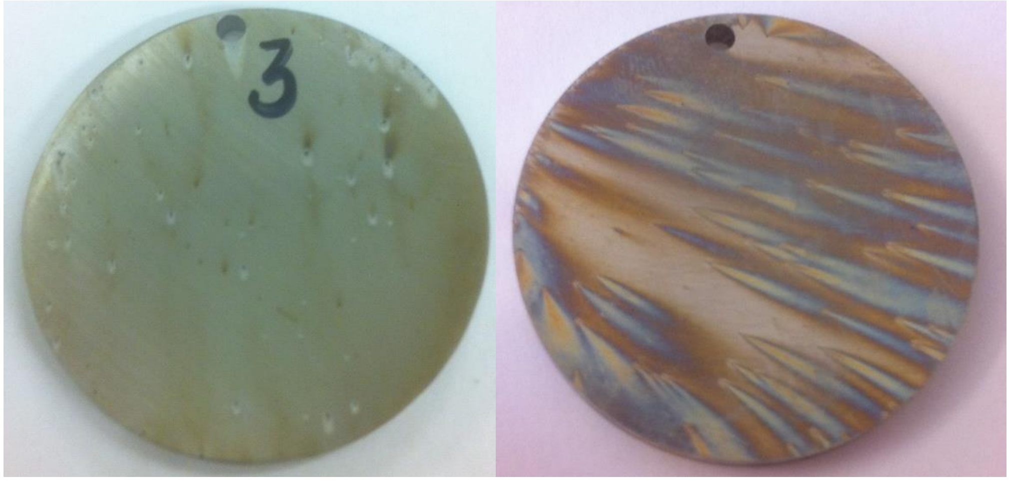
Measured OCP and pH before and after testing

	FIRST SAMPLE			**SECOND SAMPLE**		
TEST	**OCP**	**pH before**	**pH after**	**OCP**	**pH before**	**pH after**
1	-183	6,8	6,8	-105	6,8	6,8
2	-89	6,7	6,7	-223	6,9	-
3	-175	7,1	7,3	-11	7,1	7,2
4	-174	7,1	7,6	-63	7,2	7,3
5	-274	6,9	7,1	17	7,1	7,1
6	-323	7,9	8,3	-187	6,7	6,9
7	-526	6,8	8,9	-319	6,7	8,7
8	-208	6,9	8,3	-199	7,2	7,8
9	-206	6,8*	6,9*	-214	6,8*	6,9*
10	-262	6,8*	6,8*	-196	6,8*	6,8*
11	-221	6,8*	6,8*	-156	6,8*	6,8*
12	-387	7,5	8,4	7,6	7,5	7,2
13	-156	6,8*	6,8*	-209	6,8*	6,8*
14	-351	8,5	-	-157	8,4	8,3
15	-239	6,8*	6,8*	-263	6,8*	6,8*
16	-249	7,5	8,3	-323	7,5	8,4
17	-259	7,6	8,3	-194	7,7	8,2
18	-407	7,0	7,5	-324	7,0	7,4
19	-125	7,4	7,4	-198	7,4	7,6
20	-547	7,6	8,6	-337	8,3	8,5
21	-339	8,3	8,3	-243	8,2	8,2
22	-504	7,6	8,6	-136	7,7	8,8
23	-355	7,4	8,2	-242	7,4	8,3
24	-617	8,3	8,3	-505	8,3	8,6
25	-111	7,8	7,4	-551	7,8	7,6
26	43	7,6	7,8	-39	7,8	7,8
27	-166	6,8*	6,8*	-183	6,8*	6,8*
28	-115	7,2	9,1	-83	8,4	9,3
29	-138	7,4	9,0	-74	7,6	8,8
30	-348	8,7	8,4	-84	7,9	8,7
31	-32	7,1	7,2	-82	7,6	8,4
32	-326	7,4	8,3	-82	7,4	8,3

** pH-meter was broken. Reading is not valid.*

APPENDIX C PICTURES OF SAMPLES

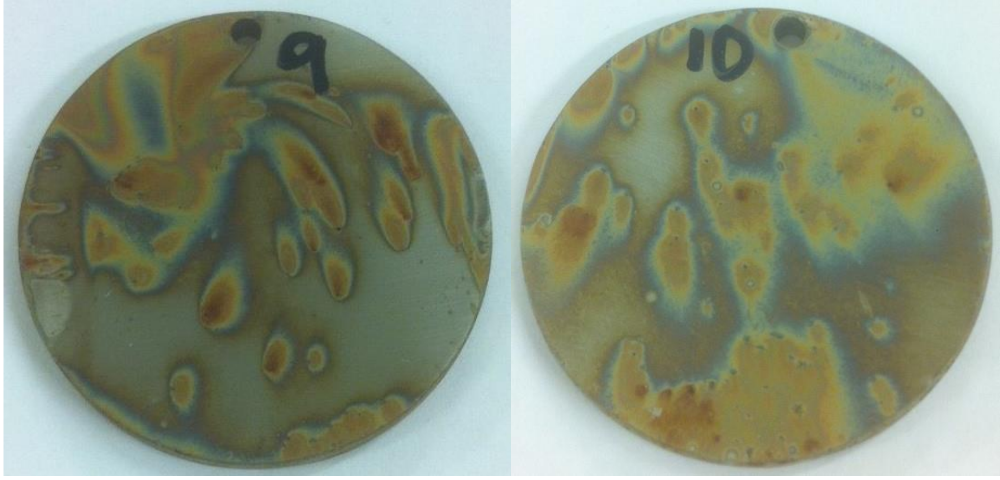
Test 1



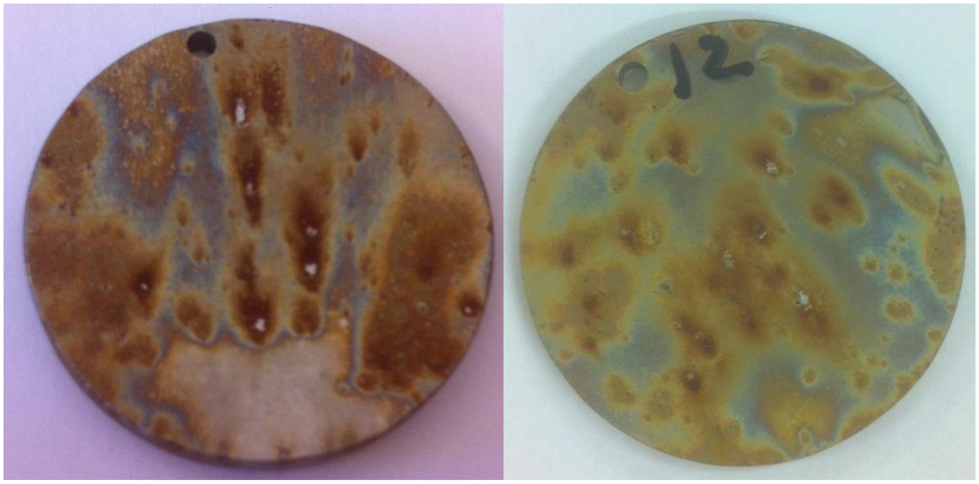
Test 2

Test 3

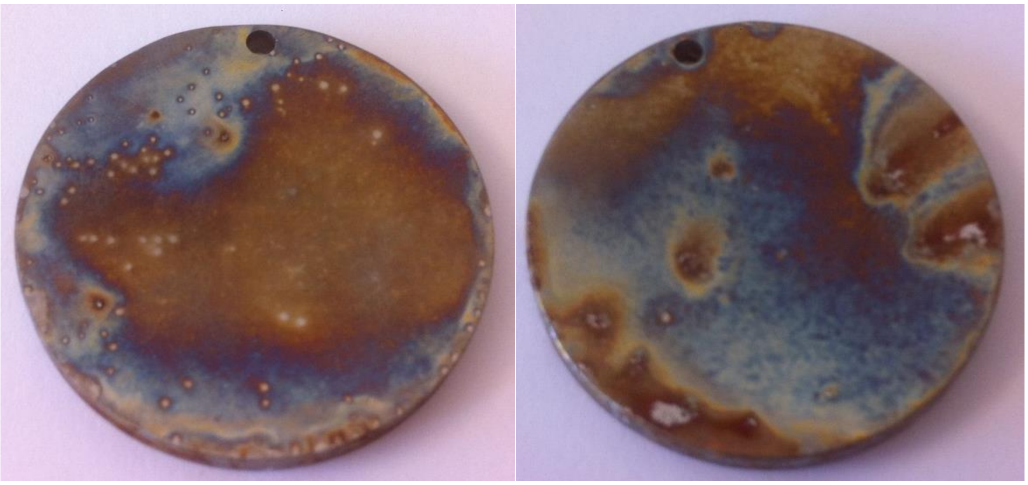
TEST 4



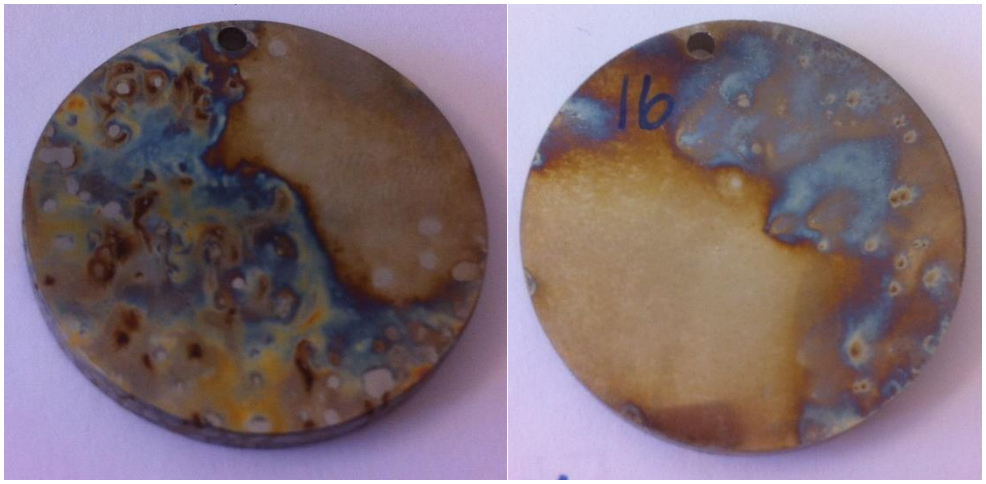
TEST 5



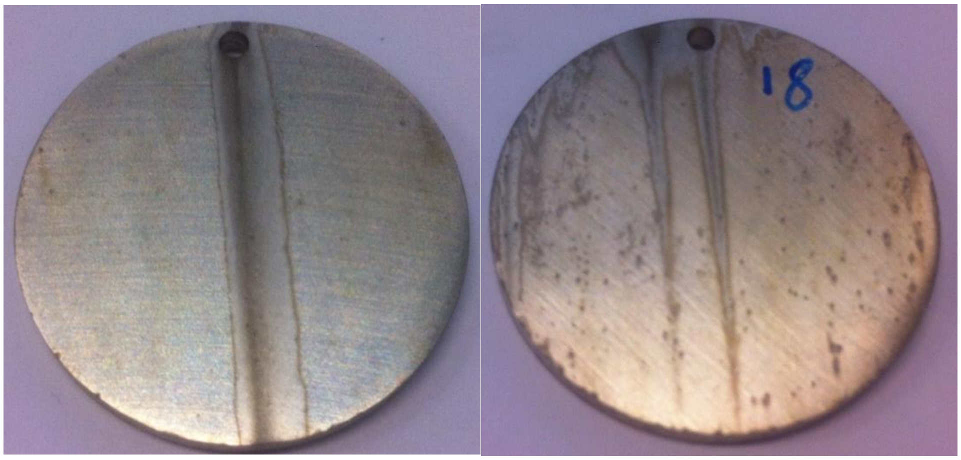
TEST 6



Test 7



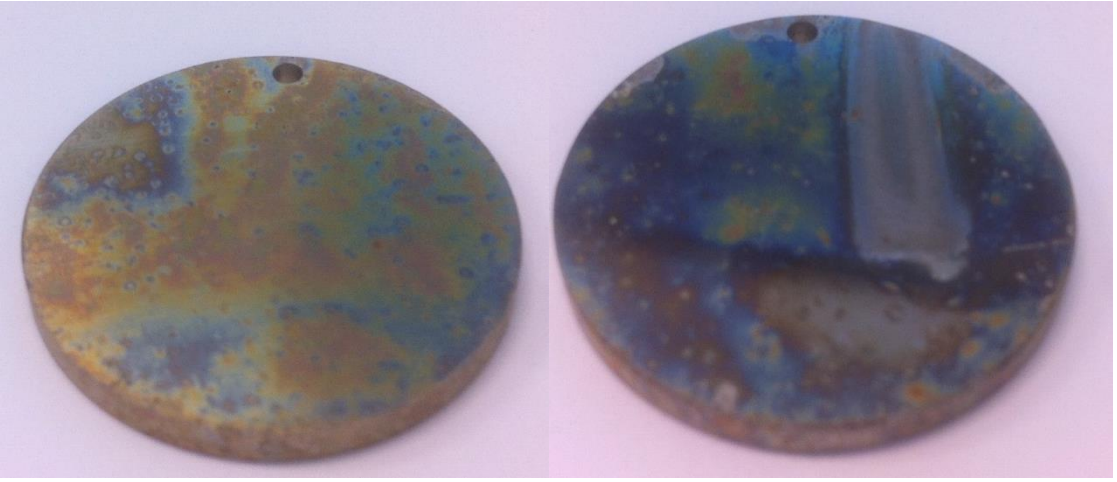
Test 8



Test 9

Test 10

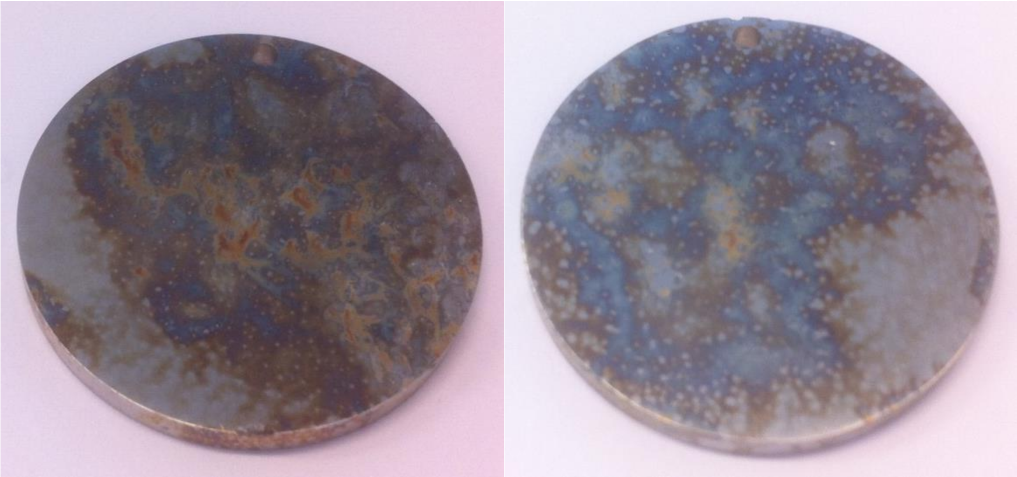
Test 11



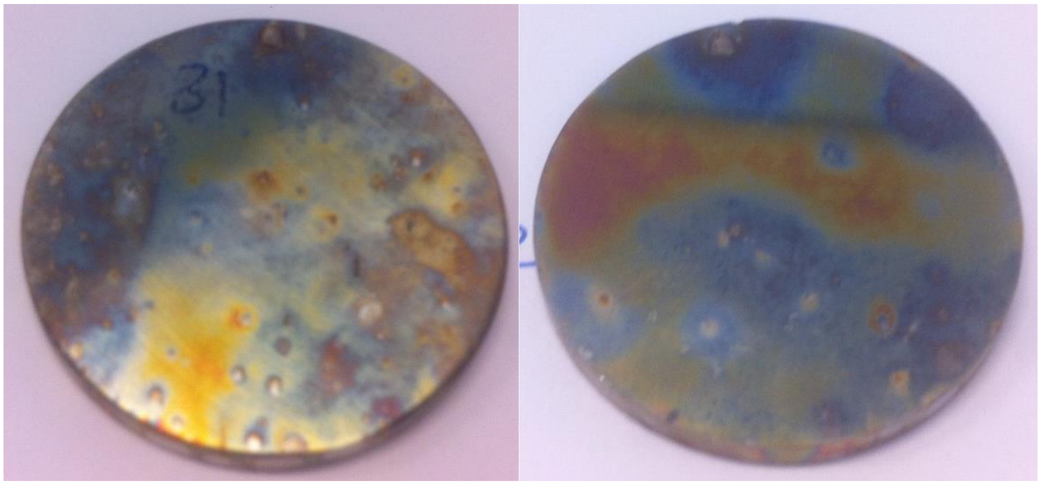
Test 12

TEST 13

TEST 14



TEST 15

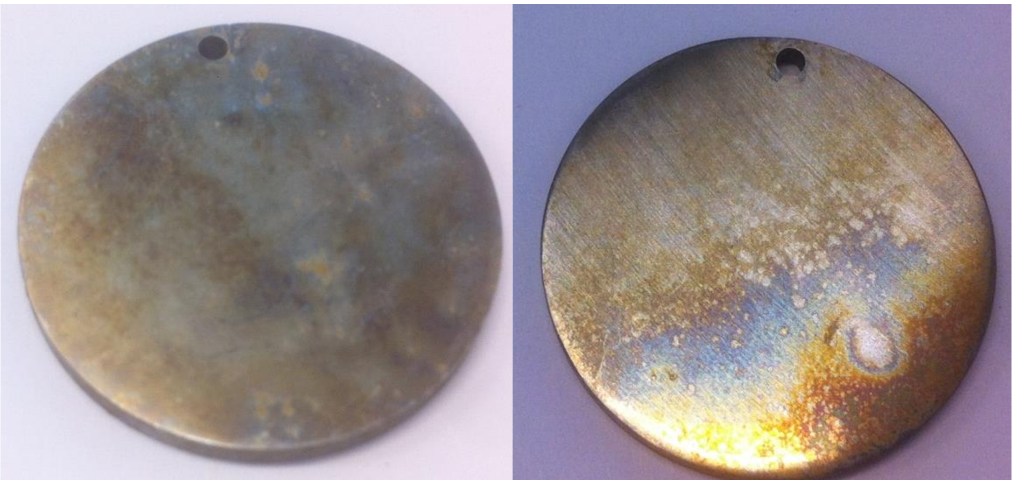


Test 16

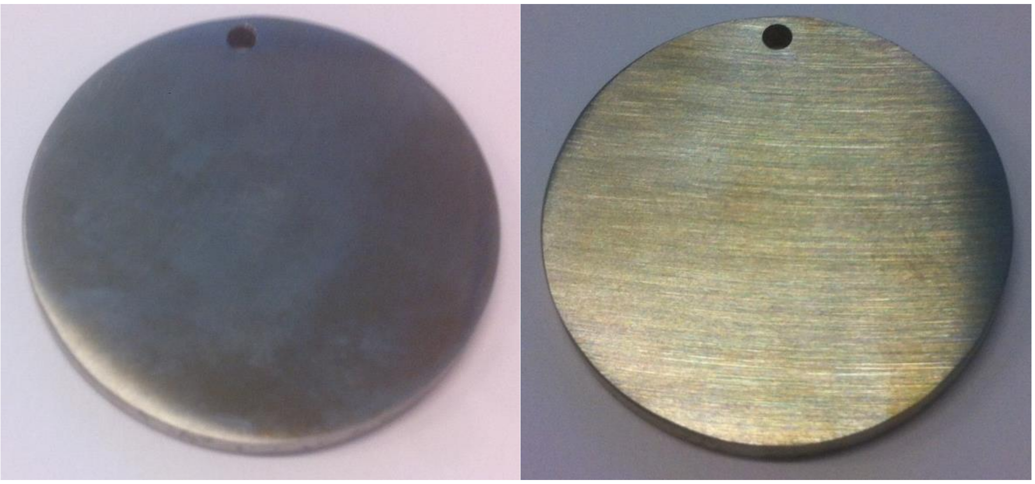
Test 17

Test 18

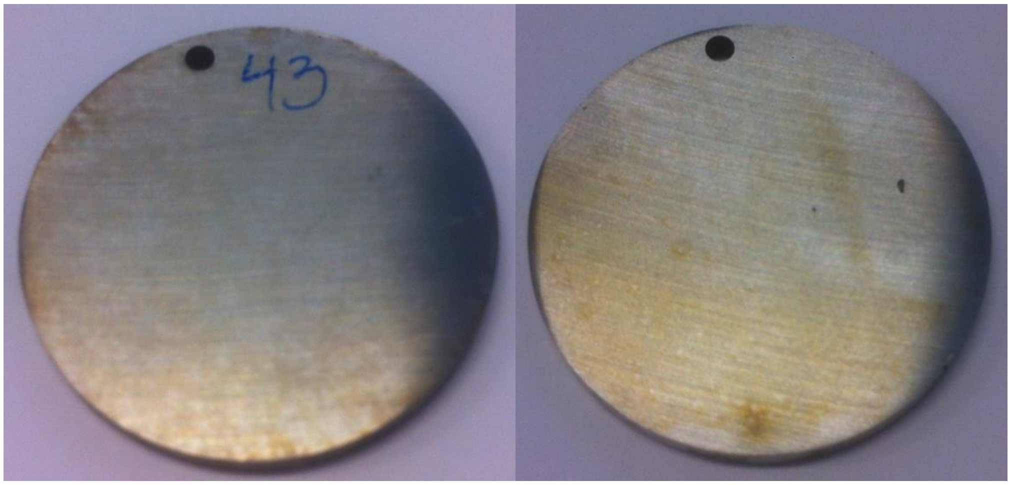
Test 19



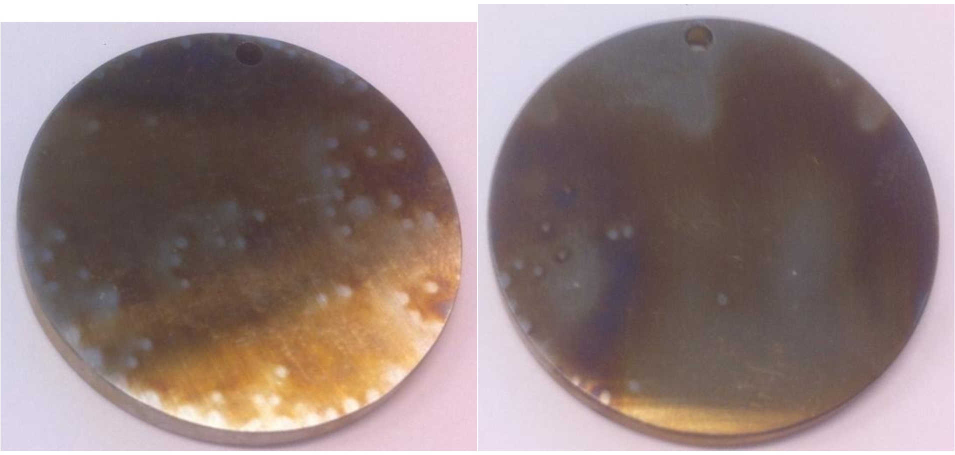
Test 20



Test 21



Test 22



Test 23

Test 24

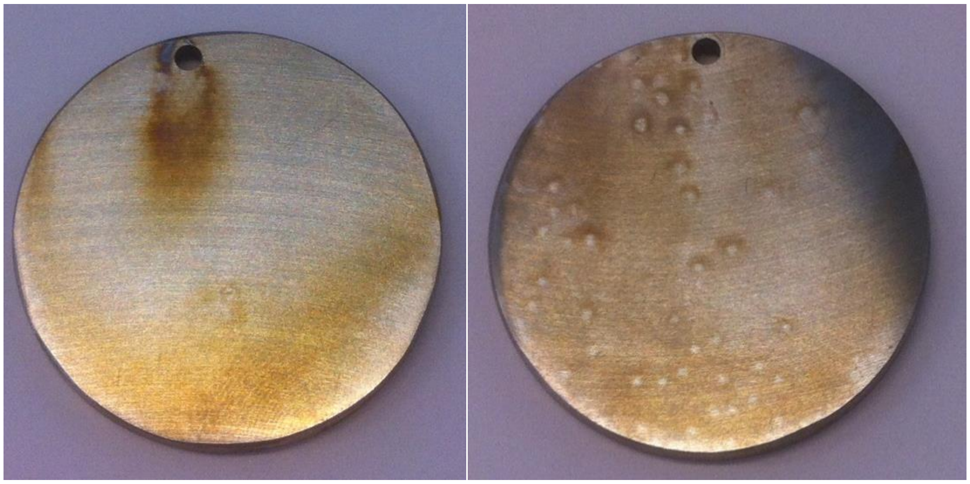
Test 25

Test 26

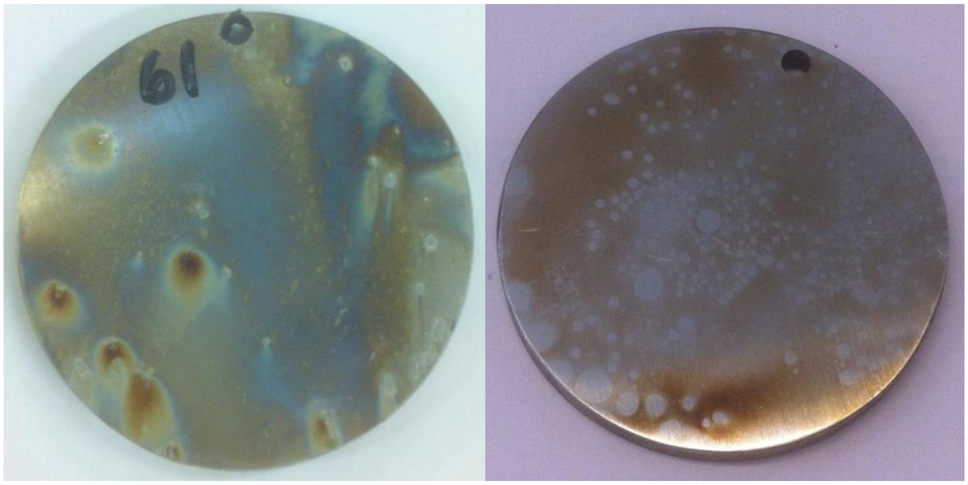
Test 27

TEST 28

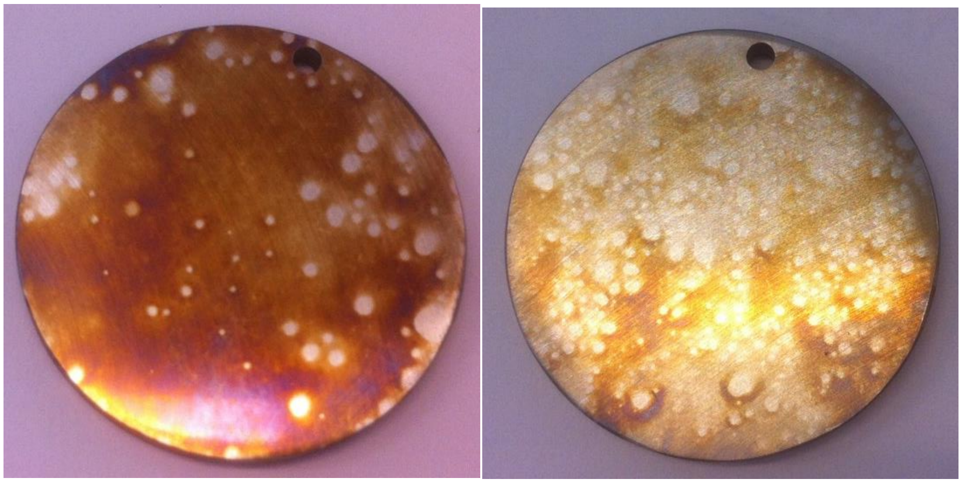
TEST 29



TEST 30



Test 31



Test 32

APPENDIX D MATERIAL DATA SHEET

SANDVIK

Datasheet updated 2013-11-28 10:24:29 (supersedes all previous editions)

Sandvik SAF 2507

(Tube and pipe, seamless)

Sandvik SAF 2507 is a super-duplex (austenitic-ferritic) stainless steel for service in highly corrosive conditions. The grade is characterized by:

- Excellent resistance to stress corrosion cracking (SCC) in chloride-bearing environments
- Excellent resistance to pitting and crevice corrosion
- High resistance to general corrosion
- Very high mechanical strength
- Physical properties that offer design advantages
- High resistance to erosion corrosion and corrosion fatigue
- Good weldability

STANDARDS

- UNS S32750
- EN number 1.4410
- EN name X 2 CrNiMoN 25-7-4
- SS 2328

Product standards
- Seamless tube and pipe: EN 10216-5
- Seamless and welded tube and pipe: ASTM A789; A790
- Flanges: ASTM A182
- Fittings: ASTM A182; (ASTM A815 applied for)
- Plate, sheet and strip: ASTM A240, EN 10088-2
- Bar steel: ASTM A479, EN 10088-3
- Forged billets: EN 10088-3

Approvals
- Approved by the American Society of Mechanical Engineers (ASME) for use in accordance with ASME Boiler and Pressure Vessel Code, Section VIII, div. 1. There is no approval for UNS S32750 in the form of plate. However, according to the ASME paragraph UG-15 it is allowed to use the design values for seamless tube according to ASME Section VIII, div. 1 also for plate.
- ASME B31.3 Chemical Plant and Petroleum Refinery piping.
- VdTÜV-Werkstoffblatt 508
- ISO 15156-3/NACE MR 0175 (Sulphide stress cracking resistant material for oil field equipment), (applies to liquid quenched tubes).
- NGS 1609 Nordic rules for application of the non-standard steel SAF 2507 manufactured by AB Sandvik Steel.

CHEMICAL COMPOSITION (NOMINAL) %

C	Si	Mn	P	S	Cr	Ni	Mo	Others
≤0.030	≤0.8	≤1.2	≤0.035	≤0.015	25	7	4	N=0.3

FORMS OF SUPPLY

Seamless tube and pipe– finishes and dimensions
Seamless tube and pipe in Sandvik SAF 2507 is supplied in dimensions up to 260 mm outside diameter. The delivery condition is solution annealed and either white pickled, or bright annealed.

Other forms of supply:
- Welded tube and pipe
- Fittings and flanges
- Wire electrodes and filler wire/rods
- Covered electrodes
- Plate, sheet and wide strip
- Bar steel
- Forged products
- Cast products

MECHANICAL PROPERTIES

The following figures apply to material in the solution annealed condition. Tube and pipe with wall thickness above 20 mm (0.787 in.) may have slightly lower values. For seamless tubes with a wall thickness <4 mm we guarantee proof strength ($R_{p0.2}$) values that are 50 MPa higher than those listed below at 20°C (68°F) as well as those listed at higher temperatures. More detailed information can be supplied on request.

At 20°C (68°F)
Tube and pipe with wall thickness max. 20 mm (0.79 in.).

METRIC UNITS

Proof strength, MPa		Tensile strength, MPa	Elongation, %		Hardness, HRC
$R_{p0.2}$ a)	$R_{p1.0}$ a)	R_m	A b)	A2"	
≥550	≥640	800-1000	≥25	≥15	≤32

IMPERIAL UNITS

Proof strength, ksi		Tensile strength, ksi	Elongation, %		Hardness, HRC
$R_{p0.2}$ a)	$R_{p1.0}$ a)	R_m	A b)	A2"	HRC
≥80	≥93	116-145	≥25	≥15	≤32

1 MPa = 1 N/mm^2

a) $R_{p0.2}$ and $R_{p1.0}$ correspond to 0.2% offset and 1.0% offset yield strength, respectively.

b) Based on $L_0 = 5.65 \sqrt{S_0}$ where L_0 is the original gauge length and S_0 the original cross-section area.

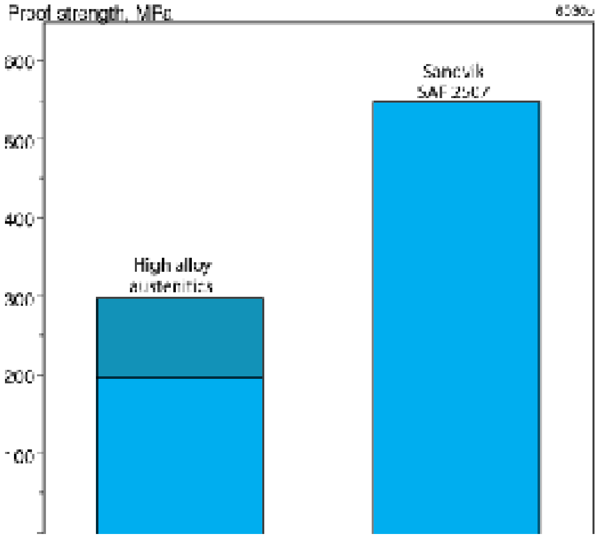


Figure 1. Comparison of minimum proof strength, 0.2% offset, of SAF 2507 and high alloy austenitic grades, for material in the solution annealed condition.

At high temperatures
If Sandvik SAF 2507 is exposed to temperatures exceeding 250°C (480°F), for prolonged periods, the microstructure changes, which results in a reduction in impact strength. This does not necessarily affect the behavior of the material at the operating temperature. For example, heat exchanger tubes can be used at higher temperatures without any problems. Please contact Sandvik for more information. For pressure vessel applications, 250°C (480°F) is required as a maximum, according to VdTÜV-Wb 508 and NGS 1609.

Tube and pipe with wall thickness max. 20 mm (0.79 in.)

METRIC UNITS

Temperature, °C	Proof strength $R_{p0.2}$, MPa min.
50	530
100	480
150	445
200	420
250	405
300	395

IMPERIAL UNITS

Temperature, °F	Proof strength $R_{p0.2}$, ksi min.
120	77.0
200	70.5
300	64.5
400	61.0
500	58.5
600	57.0

Impact strength

Sandvik SAF 2507 possesses good impact strength. The ductile brittle transition temperature is below -50°C (-58°F). The impact strength of welded Sandvik SAF 2507 is also good, although the values are lower than the base metal. The impact strength, if gas shielded arc weldments, is a minimum of 27 J (20 ft lb) at a temperature of -50°C (-58°F).

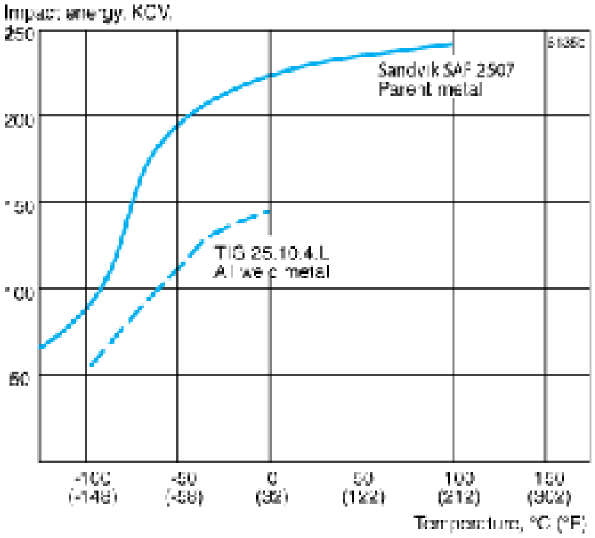


Figure 2. Typical impact energy curves for Sandvik SAF 2507 using standard Charpy V specimens (average of 3 at each temp.). Parent metal samples taken in the longitudinal direction from 260 x 12 mm bar extruded and solution annealed (1075°C / 1965°F) tube. All weld metal samples from Sandvik 25.10.4.L TIG wire.

According to ASME B31.3 the following design values are recommended for UNS S32750 (Sandvik SAF 2507):

Temperature		Stress	
°F	°C	ksi	MPa
100	38	38.7	265
200	93	35.0	240
300	149	33.1	230
400	204	31.9	220
500	260	31.4	215
600	316	31.2	215

PHYSICAL PROPERTIES

Density: 7.8 g/cm^3, 0.28 lb/in.^{3}

Specific heat capacity
Metric units Imperial units

Temperature, °C	J/(kg °C)	Temperature, °F	Btu/(lb°F)
20	490	68	0.12
100	505	200	0.12
200	520	400	0.12
300	550	600	0.13
400	585	800	0.14

Thermal conductivity

Metric units, W/(m°C)

Temperature, °C	20	100	200	300	400
Sandvik SAF 2507	14	15	17	18	20
ASTM 316L	14	15	17	18	20

Imperial units, Btu/(ft h °F)

Temperature, °F	68	200	400	600	800
Sandvik SAF 2507	8	9	10	11	12
ASTM 316L	8	9	10	10	12

Thermal expansion

Sandvik SAF 2507 has a coefficient of thermal expansion close to that of carbon steel. This gives Sandvik SAF 2507 definite design advantages over austenitic stainless steels in equipment comprising of both carbon steel and stainless steel. The values given below are average values in the temperature ranges.

METRIC UNITS, X10^{-6}/°C

Temperature, °C	30-100	30-200	30-300	30-400
Sandvik SAF 2507	13.5	14.0	14.0	14.5
Carbon steel	12.5	13.0	13.5	14.0
ASTM 316L	16.5	17.0	17.5	18

IMPERIAL UNITS, X10^{-6}/°F

Temperature, °F	86-200	86-400	86-600	86-800
Sandvik SAF 2507	7.5	7.5	8.0	8.0
Carbon steel	6.8	7.0	7.5	7.8
ASTM 316L	9.0	9.5	10.0	10.0

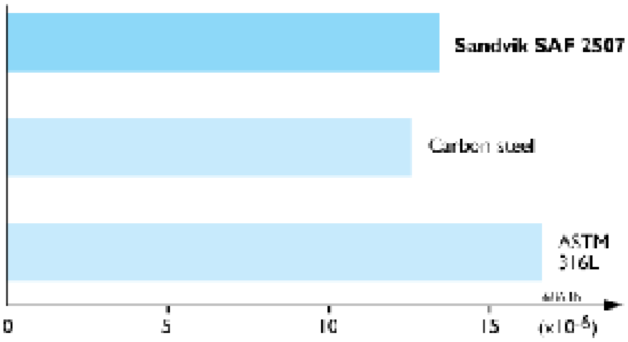


Figure 3. Thermal expansion, per°C (30-100°C, 86-210°F).

Resistivity

Temperature, °C	µΩm	Temperature, °F	µΩin.
20	0.83	68	32.7
100	0.89	200	34.9
200	0.96	400	37.9
300	1.03	600	40.7
400	1.08	800	43.2

Modulus of elasticity, (x10^{3})

METRIC UNITS AND IMPERIAL UNITS

Temperature, °C	MPa	Temperature, °F	ksi
20	200	68	29.0
100	194	200	28.2
200	186	400	27.0
300	180	600	26.2

CORROSION RESISTANCE

General corrosion
Sandvik SAF 2507 is highly resistant to corrosion by organic acids, e.g. experience less than 0.05 mm/year in 10% formic and 50% acetic acid where ASTM 316L has corrosion rate higher than 0.2 mm/year. Pure formic acid see Figure 4. Also in contaminated acid Sandvik SAF 2507 remains resistant.

Figure 5 and Figure 6 show results from tests of Sandvik SAF 2507 and various stainless steels and nickel alloys in acetic acid contaminated with chlorides which in practice are frequently present in processes.

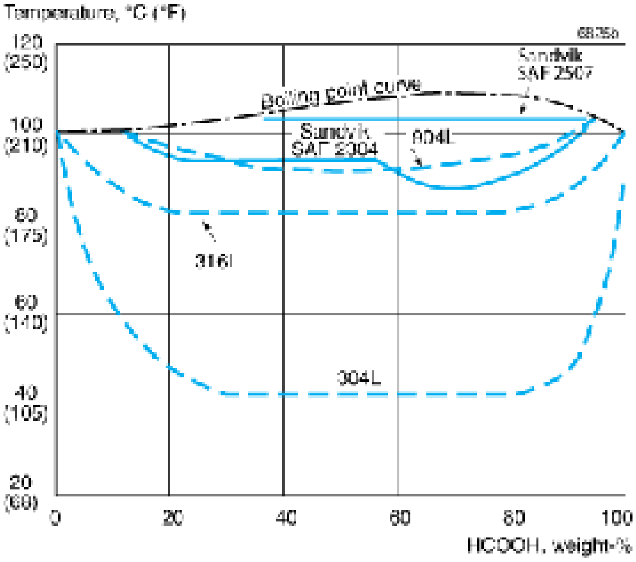


Figure 4. Isocorrosion diagram in formic acid. The curves represent a corrosion rate of 0.1 mm/year [4 mpy] in stagnant test solution.

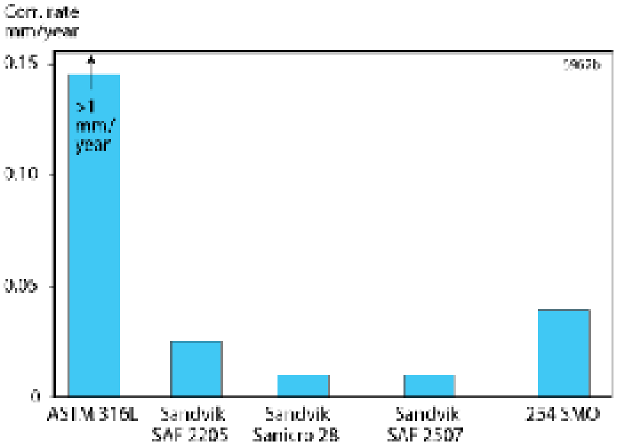


Figure 5. Corrosion rate of various alloys in 80 % acetic acid with 2000 ppm chloride ions at 90°C.

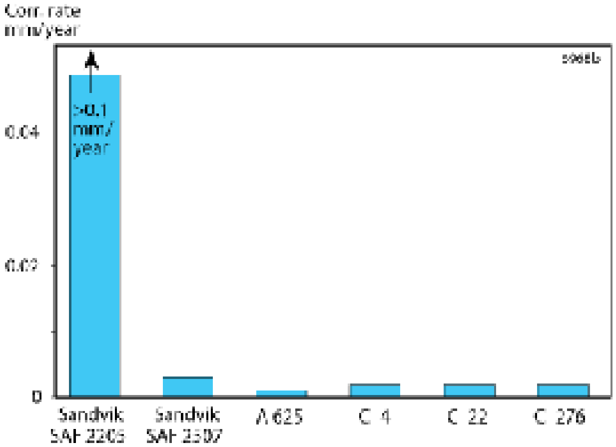


Figure 6. Corrosion rate of various alloys in concentrated acetic acid with 200 ppm chloride ions.

Practical experience with Sandvik SAF 2507 in organic acids, e.g. in terephthalic acid plants, has shown that this alloy is highly resistant to this type of environment. The alloy is therefore a competitive alternative to high alloyed austenitics and nickel alloys in applications where standard austenitic stainless steels corrode at a high rate.

Resistance to inorganic acids is comparable to, or even better than that of high alloy austenitic stainless steels in certain concentration ranges. Figures 7 to 9 show isocorrosion diagrams for sulphuric acid, sulphuric acid contaminated with 2000 ppm chloride ions, and hydrochloric acid, respectively.

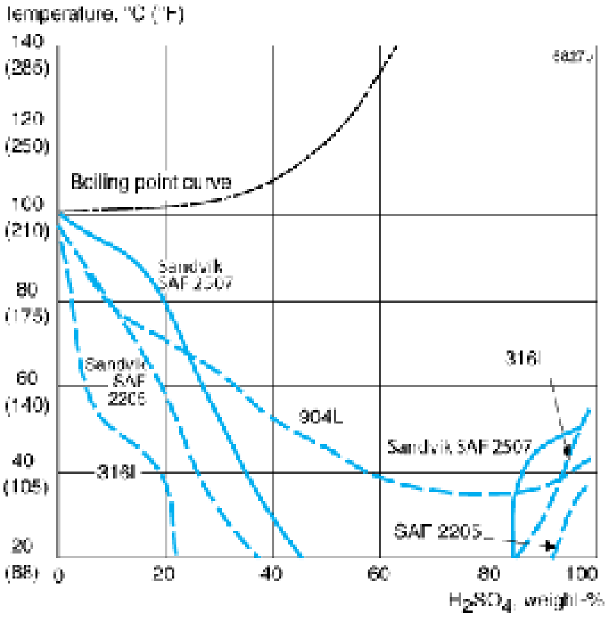


Figure 7. Isocorrosion diagram in naturally aerated sulphuric acid. The curves represent a corrosion rate of 0.1 mm/year [4 mpy] in a stagnant test solution.

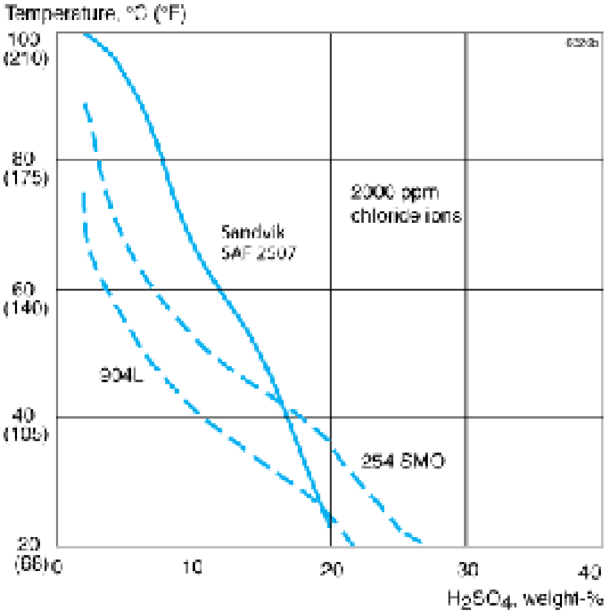


Figure 8. Isocorrosion diagram, 0.1 mm/year [4 mpy] in a naturally aerated sulphuric acid containing 2000 ppm chloride ions.

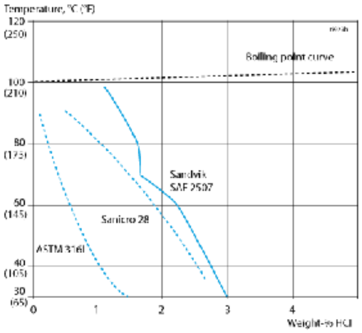


Figure 9. Isocorrosion diagram in a hydrochloric acid. The curves represent acorrosion rate of 0.1 mm/year (4 mpy) in stagnant test solution.

Pitting and crevice corrosion

The pitting and crevice corrosion resistance of stainless steel is primarily determined by the content of chromium, molybdenum and nitrogen. The manufacturing and fabrication practice, e.g. welding, are also of vital importance for the actual performance in service.

A parameter for comparing the resistance to pitting in chloride environments is the PRE number (Pitting Resistance Equivalent).
The PRE is defined as, in weight-%
PRE = %Cr + 3.3 x %Mo + 16 x %N

For duplex stainless steels the pitting corrosion resistance is dependent on the PRE value in both the ferrite phase and the austenite phase, so that the phase with the lowest PRE value will be limiting for the actual pitting corrosion resistance. In Sandvik SAF 2507 the PRE value is equal in both phases, which has been achieved by a careful balance of the elements.

The minimum PRE value for Sandvik SAF 2507 seamless tubes is 42.5. This is significantly higher than e.g. the PRE values for other duplex stainless steels of the 25Cr type which are not super-duplex. As an example UNS S31260 25Cr3Mo0.2N has a minimum PRE-value of 33.

One of the most severe pitting and crevice corrosion tests applied to stainless steel is ASTM G48, i.e. exposure to 6% $FeCl_3$ with and without crevices (method A and B respectively). In a modified version of the ASTM G48 A test, the sample is exposed for periods of 24 hours. When pits are detected together with a substantial weight loss (>5 mg), the test is interrupted. Otherwise the temperature is increased by 5 °C (9 °F) and the test is continued with the same sample. Figure 11 shows critical pitting and crevice temperatures (CPT and CCT) from the test.

Potentiostatic tests in solutions with different chloride contents are presented in Figure 11. Figure 12 shows the effect of increased acidity. In both cases the applied potential is 600 mV vs SCE, a very high value compared with that normally associated with natural unchlorinated seawater, thus resulting in lower critical temperatures compared with most practical service conditions.

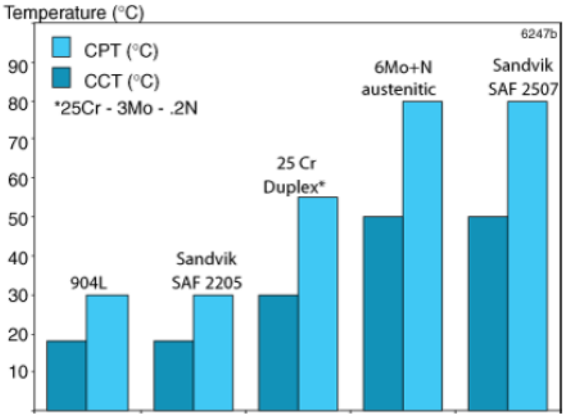


Figure 10. Critical pitting and crevice temperatures in 6% $FeCl_3$, 24h (similar to ASTM G48).

The scatter band for Sandvik SAF 2507 and *6Mo+N* illustrates the fact that both alloys have similar resistance to pitting, and CPT-values are within the range shown in the figure.

Tests were performed in natural seawater to determine the critical crevice corrosion temperature of samples with an applied potential of 150 mV vs SCE. The temperature was raised by 4°C (7°F) steps every 24 hours until crevice corrosion occurred. The results are shown in the table below.

Alloy	CCT (°C)
Sandvik SAF 2507	64
6Mo+N	61

In these tests the propagation rates of initiated crevice corrosion attacks, at 15-50°C (59-122°F) and an applied potential of 150 mV vs SCE were also determined. These were found to be around ten times lower for Sandvik SAF 2507 than for the *6Mo+N* alloy.

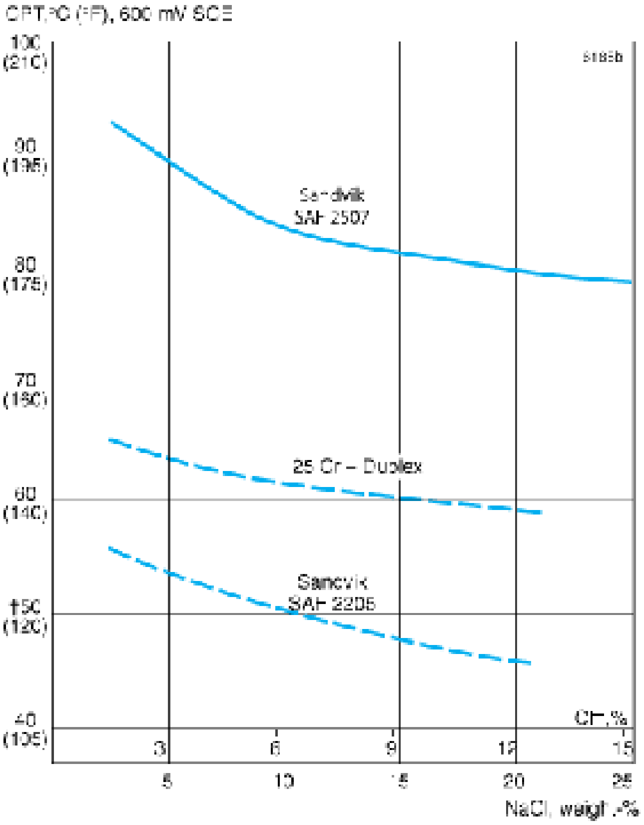


Figure 11. Critical pitting temperatures (CPT) at varying concentrations of sodium chloride, from 3 to 25% (potentiostatic determination at +600 mV SCE with surface ground with 600 grit paper).

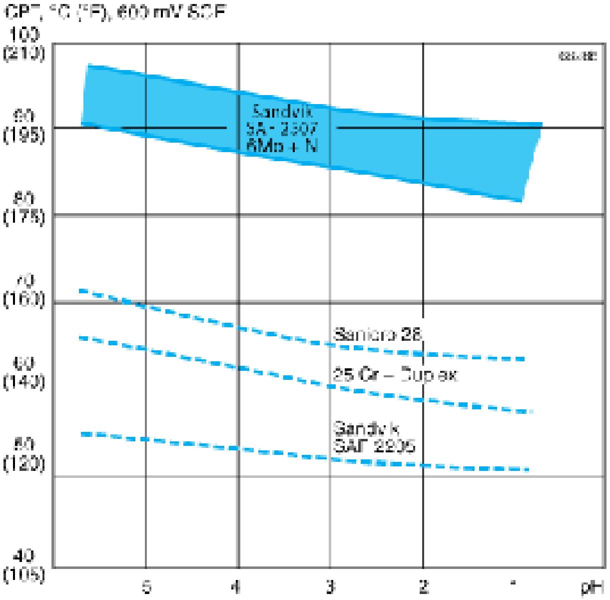


Figure 12. Critical pitting temperatures (CPT) in 3% NaCl with varying pH (potentiostatic determination at +600 mV SCE with surface ground with 600 grit paper).

The corrosion resistance of Sandvik SAF 2507 in oxidising chloride solutions is illustrated by critical pitting temperatures (CPT) determined in a 'Green death'-solution (1% $FeCl_3$ + 1% $CuCl_2$ + 11% H_2SO_4 + 1.2% HCl) and in a 'Yellow death'-solution (0.1% $Fe_2(SO_4)_3$ + 4% NaCl + 0.01 M HCl). The table below shows CPT-values for different alloys in these solutions. It is clear that the values for Sandvik SAF 2507 are on the same level as those for the nickel alloy UNS N06625. The tests demonstrate a good correlation with the ranking of alloys for use as reheater tubes in flue gas desulphurisation systems.

Critical pitting temperature (CPT) determined in different test solutions.

Alloy	Critical pitting temperature (CPT), °C 'Green death'	'Yellow death'
Sandvik SAF 2507	72.5	>90
6Mo+N	70	>90
UNS N06625	67.5	>90
ASTM 316	<25	20

Stress corrosion cracking
Sandvik SAF 2507 has excellent resistance to chloride induced stress corrosion cracking (SCC).

The SCC resistance of Sandvik SAF 2507 in chloride solutions at high temperatures is illustrated in Figure 13. There were no signs of SCC up to 1000 ppm Cl^-/300°C and 10000 ppm Cl^-/250°C.

Sandvik SAF 2507 U-bend specimens exposed for 1000 hours in hot brine (108°C, 226°F, 25% NaCl) showed no cracking.
The threshold stress for Sandvik SAF 2507 in 40% $CaCl_2$ at 100 °C (210 °F) and pH = 6.5 is above 90% of the tensile strength for both parent metal and welded joints (TIG-welded with Sandvik 25.10.4.L or MMA-welded with Sandvik 25.10.4.LR).

Figure 14 shows the result of testing in 40% $CaCl_2$ at 100 °C (210 °F) acidified to pH = 1.5. Acidifying of the standard test solution to pH = 1.5 lowers the threshold stress for Sandvik SAF 2205, but not for Sandvik SAF 2507. This applies to both parent metal and welded joints.

The threshold stress for both parent metal and welded joints of Sandvik SAF 2507 in boiling 45% $MgCl_2$, 155°C (311°F) (ASTM G36), is approximately 50% of the proof strength.

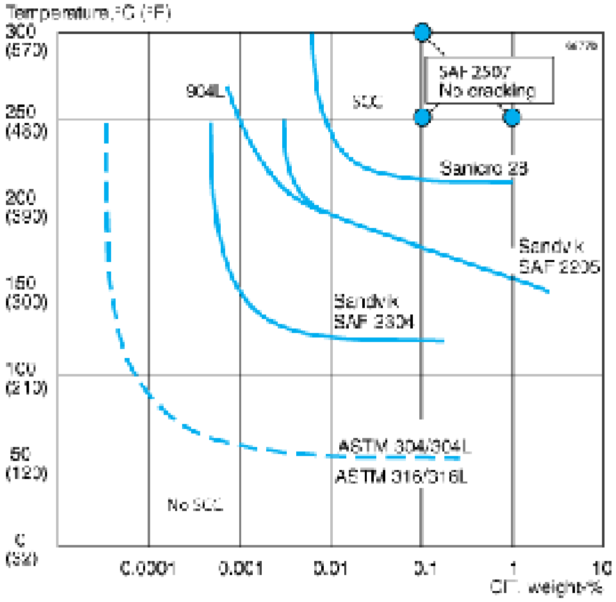


Figure 13. SCC resistance in oxygen-bearing (abt. 8 ppm) neutral chloride solutions. Testing time 1000 hours. Applied stress equal to proof strength at testing temperature.

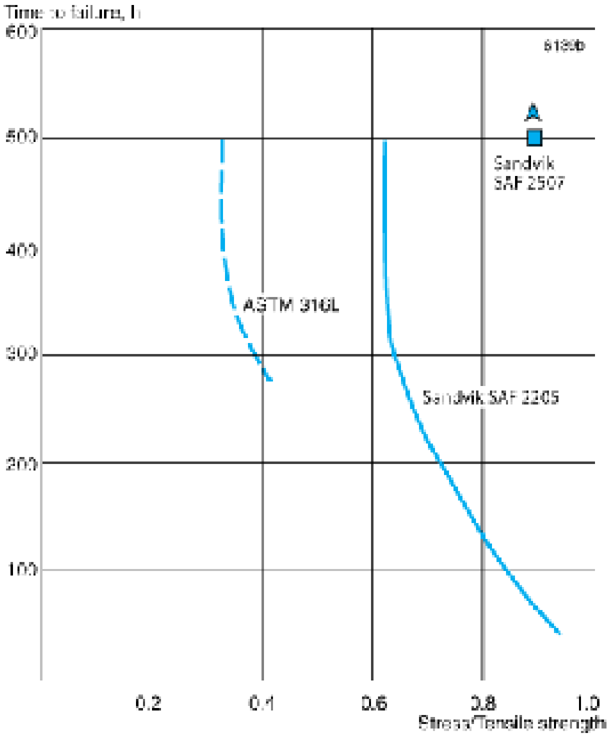


Figure 14. Results of SCC tests with constant load in 40% $CaCl_2$, pH=1.5, at 100 °C (210°F) with aerated test solution.

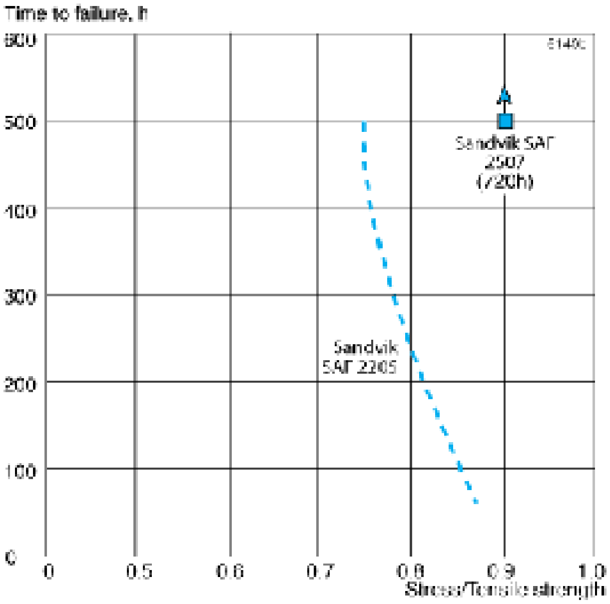


Figure 15. Constant load SCC tests in NACE solution at room temperature (NACE TM 0177).

Figure 15 shows the results of SCC tests at room temperature in NACE TM0177 Test solution A (5 % sodium chloride and 0.5 % acetic acid saturated with hydrogen sulphide). No cracking occurred on Sandvik SAF 2507, irrespective of the applied stress.

In aqueous solutions containing hydrogen sulphide and chlorides, stress corrosion cracking can also occur on stainless steels at temperatures below 60 °C (140 °F). The corrosivity of such solutions is affected by acidity and chloride content. In direct contrast to the case with ordinary chloride-induced stress corrosion cracking, ferritic stainless steels are more sensitive to this type of stress corrosion cracking than austenitic steels.

In accordance with ISO 15156/NACE MR 0175 solution annealed and liquid quenched wrought Sandvik SAF 2507 is suitable for use at temperatures up to 450 °F (232 °C) in sour environments in oil and gas production, if the partial pressure of hydrogen sulphide does not exceed 3 psi (0.20 bar).

Sandvik SAF 2507, with a maximum hardness of 32 HRC, solution annealed and rapidly cooled, according to NACE MR0103, is suitable for use in sour petroleum refining.

Intergranular corrosion

Sandvik SAF 2507 is a member of the family of modern duplex stainless steels whose chemical composition is balanced to give quick reformation of austenite in the high temperature heat affected zone of a weld. This results in a microstructure that provides the material with good resistance to intergranular corrosion. Sandvik SAF 2507 passes testing to ASTM A262 Practice E (Strauss test) without reservation.

Erosion corrosion

The mechanical properties combined with corrosion resistance give Sandvik SAF 2507 a good resistance to erosion corrosion. Testing in sand containing media has shown that Sandvik SAF 2507 has an erosion corrosion resistance better than corresponding austenitic stainless steels. Figure 16 below shows the relative mass loss rate of the duplex Sandvik SAF 2507, Sandvik SAF 2205 and an austenitic 6Mo+N type steel after exposure to synthetic seawater (ASTM D-1141) containing 0.025-0.25 % silica sand at a velocity of 8.9-29.3 m/s (average of all tests is shown).

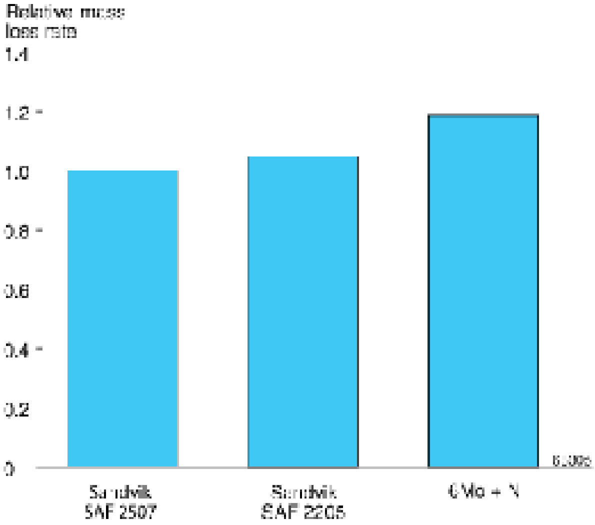


Figure 16. Relative mass loss rate after testing of the resistance against erosion corrosion.

Corrosion fatigue
Duplex stainless steels which have a high tensile strength usually have a high fatigue limit and high resistance to both fatigue and corrosion fatigue.

The high fatigue strength of Sandvik SAF 2507 can be explained by its good mechanical properties, while its high resistance to corrosion fatigue has been proven by fatigue testing in corrosive media.

HEAT TREATMENT

The tubes are normally delivered in heat treated condition. If additional heat treatment is needed due to further processing the following is recommended.

Solution annealing

1050-1125°C (1920-2060°F), rapid cooling in air or water.

WELDING

The weldability of Sandvik SAF 2507 is good. Suitable welding methods are manual metal-arc welding with covered electrodes or gas-shielded arc welding. Welding should be undertaken within the heat input range of 0.2-1.5 kJ/mm and with an interpass temperature of 150°C (300°F) maximum.

Preheating or post-weld heat treatment is not necessary.

Matching filler metals are recommended in order to obtain a weld metal with optimum corrosion resistance and mechanical properties. For gas-shielded arc welding use Sandvik 25.10.4.L, and for manual metal-arc welding the covered electrode Sandvik 25.10.4.LR.

FABRICATION

Bending
The starting force needed for bending is slightly higher for Sandvik SAF 2507 than for standard austenitic stainless steels (ASTM 304L and 316L).

If the service conditions are on the limit of the stress corrosion resistance of Sandvik SAF 2507 heat treatment is recommended after cold bending. For pressure vessel applications in Germany and the Nordic countries heat treatment may be required after cold deformation in accordance with VdTÜV-Wb 508 and NGS 1609. Heat treatment should be carried out by solution annealing (See under Heat treatment) or resistance annealing.

Hot bending is carried out at 1125-1025°C (2060-1880°F) and should be followed by solution annealing.

Expanding
Compared to austenitic stainless steels, Sandvik SAF 2507 has a higher proof and tensile strength. This must be kept in mind when expanding tubes into tubesheets. Normal expanding methods can be used, but the expansion requires higher initial force and should be undertaken in one operation. As a general rule, tube to tubesheet joints should be welded if the service conditions include a high chloride concentration, thus

limiting the risk of crevice corrosion.

Machining

Being a two-phase material (austenitic-ferritic) Sandvik SAF 2507 will present a different tool wear profile from that of single-phase steels of type ASTM 304L. The cutting speed must therefore be lower than that recommended for ASTM 304L. It is recommended that a tougher insert grade is used than when machining austenitic stainless steels, e.g. ASTM 304L.

APPLICATIONS

Sandvik SAF 2507 is a duplex stainless steel especially designed for service in aggressive chloride-containing environments. Typical applications are:

TYPICAL APPLICATIONS FOR SANDVIK SAF 2507

Oil and gas exploration and production	Chloride-containing environments such as seawater handling and process systems. Hydraulic and process fluid tubes in umbilicals
Seawater cooling	Tubing for heat exchangers in refineries, chemical industries, process industries and other industries using seawater or chlorinated seawater as coolant
Salt evaporation	Evaporator tubing for production of corrosive salts, e.g. chlorides, sulphates and carbonates
Desalination plants	Pressure vessels for reverse osmosis units, tube and pipe for seawater transport, heat exchanger tubing
Geothermal wells	Heat exchangers in geothermal exploitation units, systems exposed to geothermal or high salinity brines, tubing and casing for production
Oil refining and petrochemical and gas processing	Tubes and pipes where the process environment contains a high amount of chlorides, or is contaminated with hydrochloric acid
Pulp and paper production	Material for chloride-containing bleaching environments
Chemical processing	Organic acid plants, also when process solutions are contaminated with e.g. chlorides
Mechanical components requiring high strength	Propeller shafts and other products subjected to high mechanical load in seawater and other chloride-containing environments
Desulphurisation units	As reheater tubes in flue gas desulphurisation systems. The good mechanical and corrosion properties make Sandvik SAF 2507 an economical choice in many applications by reducing the life cycle cost of equipment.

APPENDIX E PROBLEM DESCRIPTION AND RISK ANALYSIS

THE NORWEGIAN UNIVERSITY
OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF ENGINEERING DESIGN
AND MATERIALS

MASTER THESIS SPRING 2014
FOR
STUD.TECHN. MONIKA NÆSS

EFFECT OF MICROSTRUCTURE AND SURFACE FINISH ON LOCALIZED CORROSION PERFORMANCE OF SUPER DUPLEX STAINLESS STEELS IN SEAWATER

Effekt av mikrostruktur og overflatefinish på lokal korrosjon av super dupleks rustfritt stål i sjøvann

BACKGROUND

Corrosion resistant alloys (CRAs) used in subsea pressure-retaining components must be compatible with production fluids and resistant to pitting and crevice corrosion in seawater. Whereas materials selection in production environments is governed by well-established international standards such as ISO 15156, much debate still exists as of how to determine the maximum allowable seawater service temperature. Most industry specifications rely on the ASTM G48 standard to determine localized corrosion resistance. However, for 22% Cr duplex and 25% Cr super-duplex stainless steels (DSS and SDSS, respectively) there is no consensus on surface finish prior testing (e.g. grinding or pickling) and test temperature (e.g. 50^0C in NORSOK 630 versus 40^0C in ASTM A923). Moreover, testing is conducted in a 6% ferric chloride (pH 1.30) or a 6% ferric chloride + 1% hydrochloric acid (pH 0.4) solution, which may lead to a gross underestimation of the actual critical pitting temperature (CPT) in seawater. Underestimating CPT will result in a very conservative material selection criterion, increasing materials and manufacturing costs.

OBJECTIVE

The main objective of the Master project will be to: *quantify the seawater pitting corrosion resistance of a SDSS and its correlation with: i) alloy's microstructure and ii) surface finish before testing.*

SCOPE-OF-WORK

This master project will determine the maximum allowable seawater temperature of SDSS. This will be accomplished by evaluating corrosion, pitting and re-passivation potentials (E_{Corr}, E_{Pit}, and E_{Rep}, respectively) as well as passive current densities (i_{Pass}) determined by the cyclic potentiodynamic polarization (CPP) test as a function of microstructure, test temperature, and sample preparation procedures. ASTM G61 shall be used as a guideline.

Materials

One SDSS alloy will be tested – but with two metallurgical conditions – i) base material (solution annealed + water quenched) and ii) heat treated to introduce sigma phase precipitations.

Surface finish

Two different surface finishes will be evaluated; i) pickling according to NORSOK M-630 (5 min. at 60^0C in a solution of 20% HNO_3 + 5% HF) and ii) wet grinding 120-grit SiC paper or equivalent, allowing samples to dry in a desiccator 24 hour prior to testing.

Electrolyte
The electrochemical tests will be done in 3.5% NaCl solution. The temperature range will be from room temperature and up to 90^0C.

Analysis
After exposure selected surfaces shall be examined in light microscope and/or SEM to describe the corrosion attacks. For some samples also EDS/EDX can be used to determine chemical composition in a corrosion region.

The following activities will be executed in the project (*can be revised during the project*):

- Execute a literature survey to establish the state of knowledge on localized corrosion of SDSS in chloride containing (seawater) environment. Special attention shall be given to the effect of microstructure, second phase precipitation, and surface finish.
- Develop a detailed test program for the experimental part of the project including heat treatment, characterization of microstructure, electrochemical testing.
- Execute the test program
- Evaluate the outcome from the experimental work and make conclusions and recommendations.

Three weeks after start of the thesis work, an A3 sheet illustrating the work is to be handed in. A template for this presentation is available on the IPM's web site under the menu "Masteroppgave" (http://www.ntnu.no/ipm/masteroppgave). This sheet should be updated one week before the Master's thesis is submitted.

Performing a risk assessment of the planned work is obligatory. Known main activities must be risk assessed before they start, and the form must be handed in within 3 weeks of receiving the problem text. The form must be signed by your supervisor. All projects are to be assessed, even theoretical and virtual. Risk assessment is a running activity, and must be carried out before starting any activity that might lead to injury to humans or damage to materials/equipment or the external environment. Copies of signed risk assessments should also be included as an appendix of the finished project report.

The thesis should include the signed problem text, and be written as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents, etc. During preparation of the text, the candidate should make efforts to create a well arranged and well written report. To ease the evaluation of the thesis, it is important to cross-reference text, tables and figures. For evaluation of the work a thorough discussion of results is appreciated.

The thesis shall be submitted electronically via DAIM, NTNU's system for Digital Archiving and Submission of Master's thesis.

This project will be run in close cooperation with GE Oil & Gas. Contact person is Mariano Iannuzzi (E-mail: mariano.iannuzzi@ge.com)

Torgeir Welo
Head of Division

Roy Johnsen
Professor/Supervisor

NTNU
Norges teknisk-
naturvitenskapelige universitet
Institutt for produktutvikling
og materialer

NTNU

HMS

Kartlegging av risikofylt aktivitet

Utarbeidet av	Nummer	Dato
HMS-avd.	HMSRV2601	22.03.2011
Godkjent av		Erstatter
Rektor		01.12.2006

Enhet: IPM **Dato: 20.01.14**

Linjeleder: Roy Johnsen

Deltakere ved kartleggingen (m/ funksjon):
(Ansv. veileder, student, evt. medveiledere, evt. andre m. kompetanse)

Kort beskrivelse av hovedaktivitet/hovedprosess: Masteroppgave student Monika Næss: Effect of microstructure and surface finish on localized corrosion performance of Super Duplex Stainless steels in seawater.

Er oppgaven rent teoretisk? (JA/NEI)**: Nei**

Signaturer: *Ansvarlig veileder: Roy Johnsen* *Student: Monika Næss* Monika Næss

ID nr.	Aktivitet/prosess	Ansvarlig	Eksisterende dokumentasjon	Eksisterende sikringstiltak	Lov, forskrift o.l.	Kommentar
1	Slipe prøver	Monika Næss	NTNUs interne instruks for bruk av slipemaskin	Prøveholder for sliping og personlig verneutstyr.	Arbeidsmiljøloven § 3-2, 1. ledd: Arbeidsgiveren skal "sørge for at arbeidstakerne gjøres kjent med ulykkes- og helsefarer som kan være forbundet med arbeidet, og at de får den opplæring, øvelse og instruksjon som er nødvendig	
2	Etsing med 20% HNO_3 + 5% HF løsning	Monika Næss	Datablad for kjemikalier og instruks for arbeid på NTNUs laboratorier	HMS Datablad og spesielt personlig verneutstyr tilpasset Flussyre	Arbeid med brannfarlige, eksplosive eller helsefarlige stoffer og produkter § 12 og § 14 i kjemikalieforskriften og § 4-5.Særlig om kjemisk og biologisk helsefare	Utføres av sertifisert operatør John Erik Lein, Sintef

3	Forsøk i vann ved høye temperaturer	Monika Næss		Personlig verneutstyr	n.a.	
4	Bruk av nitrogengass i forsøk	Monika Næss		O_2-måler	n.a.	
5	Varmebehandle prøver på 875°C	Monika Næss	NTNUs interne instrukser	Spesialhansker, labfrakk, vernebriller		
6	Skrive prosjektrapport	Monika Næss			§ 4-1.Generelle krav til arbeidsmiljøet	

NTNU	Risikomatrise	utarbeidet av	Nummer	Dato
		HMS-avd.	HMSRV2604	08.03.2010
		godkjent av		Erstatter
HMS/KS		Rektor		09.02.2010

Enhet: IPM

Dato:

Linjeleder:

Deltakere ved kartleggingen (m/ funksjon): Roy Johnsen, Veileder og Monika Næss, Student
(Ansv. Veileder, student, evt. medveiledere, evt. andre m. kompetanse)

Risikovurderingen gjelder hovedaktivitet: Masteroppgave student Monika Næss. Effect of microstructure and surface finish on localized corrosion performance of Super Duplex Stainless steels in seawater.

Signaturer: *Ansvarlig veileder: Roy Johnsen* *Student: Monika Næss* Monika Næss

ID nr	Aktivitet fra kartleggings-skjemaet	Mulig uønsket hendelse/ belastning	Vurdering av sannsyn-lighet	Vurdering av konsekvens:				Risiko-Verdi (menn-eske)	Kommentarer/status Forslag til tiltak
			(1-5)	Menneske (A-E)	Ytre miljø (A-E)	Øk/ materiell (A-E)	Om-dømme (A-E)		
1	Slipe prøver	Skade på fingre ved bruk av slipemaskin	3	A				A3	Bruk riktig verneutstyr og kloss for å holde prøven under sliping
2	Etsing med 20% HNO_3 + 5% HF løsning	Hud eller øyne eksponert for kjemikalier	2	A				A2	Følg instruks fra HMS databad og laboratoriets interne retningslinjer
		Innånding av farlige kjemikalier	2	B				B2	Jobb under avtrekk og følg HMS Datablad
		Kjemikalier kastes i vasken	2	A	B			A3	Følg anvisninger om retur av kjemikalier
3	Forsøk i vann ved høye temperaturer	Brannskader ved søl av varmt vann	3	C				C3	La vannet avkjøles før håndtering og vis forsiktighet.

4	Bruk av nitrogengass i forsøk	Lekkasje av nitrogengass kan fortrenge oksygen og forårsake kvelning. Spesielt i trange rom.	2	B				B2	Oksygenmåler bør være tilgjengelig på arbeidsplassen.
5	Varmebehandling av prøver ved 875°C	Fare for brannskader	2	B				B2	Bruk riktig verneutstyr og vis forsiktighet.
6	Skrive prosjektrapport	Stress og belastningsskader	3	A				A3	Ta pauser og endre sittestilling

Sannsynlighet vurderes etter følgende kriterier:

Svært liten 1	Liten 2	Middels 3	Stor 4	Svært stor 5
1 gang pr 50 år eller sjeldnere	1 gang pr 10 år eller sjeldnere	1 gang pr år eller sjeldnere	1 gang pr måned eller sjeldnere	Skjer ukentlig

Konsekvens vurderes etter følgende kriterier:

Gradering	Menneske	Ytre miljø Vann, jord og luft	Øk/materiell	Omdømme
E Svært Alvorlig	Død	Svært langvarig og ikke reversibel skade	Drifts- eller aktivitetsstans >1 år.	Troverdighet og respekt betydelig og varig svekket
D Alvorlig	Alvorlig personskade. Mulig uførhet.	Langvarig skade. Lang restitusjonstid	Driftsstans > ½ år Aktivitetsstans i opp til 1 år	Troverdighet og respekt betydelig svekket
C Moderat	Alvorlig personskade.	Mindre skade og lang restitusjonstid	Drifts- eller aktivitetsstans < 1 mnd	Troverdighet og respekt svekket
B Liten	Skade som krever medisinsk behandling	Mindre skade og kort restitusjonstid	Drifts- eller aktivitetsstans < 1uke	Negativ påvirkning på troverdighet og respekt
A Svært liten	Skade som krever førstehjelp	Ubetydelig skade og kort restitusjonstid	Drifts- eller aktivitetsstans < 1dag	Liten påvirkning på troverdighet og respekt

Risikoverdi = Sannsynlighet x Konsekvens
Beregn risikoverdi for Menneske. Enheten vurderer selv om de i tillegg vil beregne risikoverdi for Ytre miljø, Økonomi/materiell og Omdømme. I så fall beregnes disse hver for seg.

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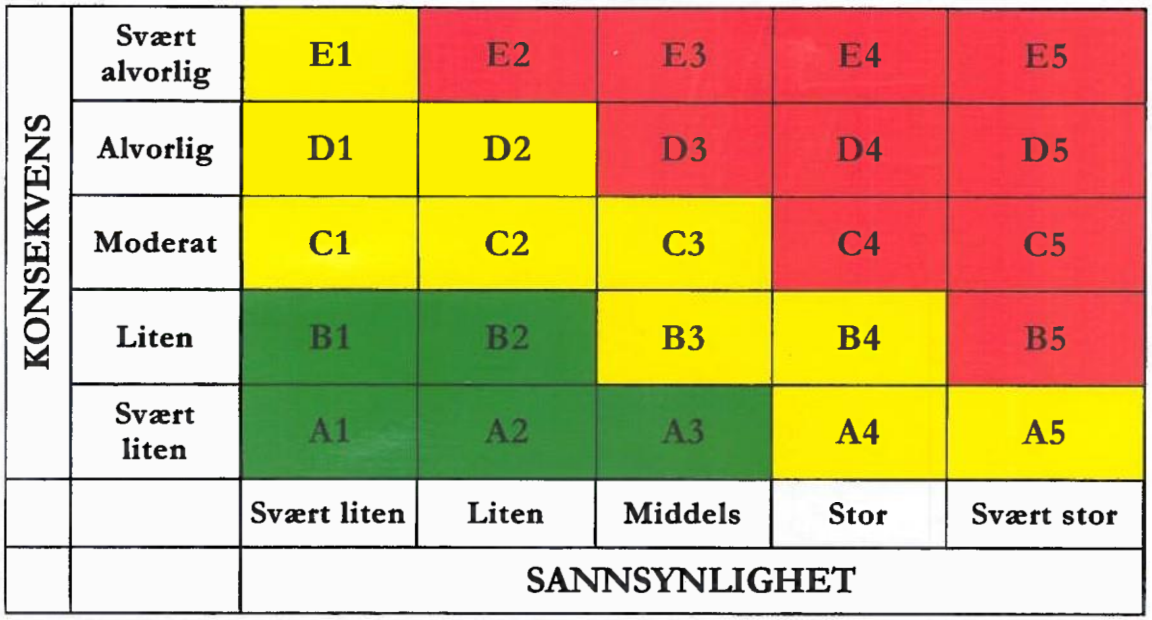
Til kolonnen "Kommentarer/status, forslag til forebyggende og korrigerende tiltak":
Tiltak kan påvirke både sannsynlighet og konsekvens. Prioriter tiltak som kan forhindre at hendelsen inntreffer, dvs. sannsynlighetsreduserende tiltak foran skjerpet beredskap, dvs. konsekvensreduserende tiltak.

MATRISE FOR RISIKOVURDERINGER ved NTNU



KONSEKVENS	Svært alvorlig	E1	E2	E3	E4	E5
	Alvorlig	D1	D2	D3	D4	D5
	Moderat	C1	C2	C3	C4	C5
	Liten	B1	B2	B3	B4	B5
	Svært liten	A1	A2	A3	A4	A5
		Svært liten	Liten	Middels	Stor	Svært stor
		SANNSYNLIGHET				

Prinsipp over akseptkriterium. Forklaring av fargene som er brukt i risikomatrisen.

Farge		Beskrivelse
Rød	🟥	Uakseptabel risiko. Tiltak skal gjennomføres for å redusere risikoen.
Gul	🟨	Vurderingsområde. Tiltak skal vurderes.
Grønn	🟩	Akseptabel risiko. Tiltak kan vurderes ut fra andre hensyn.