Comparing critical pitting temperatures of stainless steels measured electrochemically in NaCl and $MgCl_2$ solutions

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Abstract

Localised corrosion, such as pitting and crevice corrosion, is the most common reason to failure in stainless steels. Available standardized methods to rank stainless steels, for example measuring the critical pitting corrosion temperature, CPT, according to ASTM G150, are restricted in measuring pitting corrosion properties for e.g. hyper duplex and superaustenitic stainless steels, due to their high pitting corrosion resistance. In order to rank these materials, a testing temperature above the boiling point in NaCl, i.e. 100°C, is necessary. Alloys with CPT above or just below the boiling point of an aqueous solution of 1M NaCl can therefore not be evaluated.

This work attempts to investigate and compare alloys and their CPT, in two different solutions. One set of measurements was carried out in the standard solution, 1M NaCl and the other set in 3M $MgCl_2$. The CPT values for the different solutions were then compared and discussed. By using magnesium chloride salt, the boiling point was increased, which enabled measurements to rank high alloyed stainless steels with CPT above the boiling point in the standard solution.

Keywords: pitting corrosion, critical pitting temperature, CPT, high alloyed stainless steels, duplex stainless steel, austenitic stainless steels, superaustenitic stainless steel, hyper duplex stainless steels, electrolytes

1 Introduction

The concept of critical pitting temperature was developed in the 1970s by Brigham and Tozer [1]. The ability to rank stainless steel grades by using the temperature as the only parameter, independently of the redox and corrosion potential, has been used for many years in development of new stainless steel grades. The CPT is considered to be independent of the chloride content in a certain range, for example as prescribed in the ASTM G 150 [2]. But a parameter which influences the CPT value is the surface roughness. For example, Moyaed et al demonstrated that a smoother surface (3µm finish) caused a higher measured CPT than a rough surface (60 grit) [3].

The choice of using magnesium chloride in this work was mainly based on the ability of the solution to reach a higher temperature due to its higher boiling point. Data on the relationship of concentrations and boiling points of aqueous magnesium chloride solutions is available in the ASTM G36 standard [4]. However, the change from Na^+ to Mg^{2+} cation may influence the results. At present time there is no detailed mechanism for different cations and their influence on the CPT temperatures in 3M of $MgCl_2$. However, recent data from measurements in boiling magnesium chloride at 155°C and 45 wt-% (7.4M) show that the magnesium ion can be incorporated in the passive film. These findings were related to stress corrosion cracking and not pitting corrosion [5]. Nevertheless, this is an indication of limit in the use of $MgCl_2$ salt in higher concentrations and by increasing the temperature even further it indicates a risk of changing the corrosion mechanism.

Ernst and Newman showed that there was an effect of different cations on the pit solution chemistry by artificial pit technique [6]. They showed that the dependence of CPT in relation to the concentrations of two different salts, NaCl and $CaCl_2$ varied differently with respect to linearity and salt. Qvarfort presented that the CPT does not depend on chloride concentration in a certain range, but does fall at very high chloride concentrations [7]. An explanation is that the stability of a pit depends on the concentrations of the hydrolyzing alloy, metal cations and the chloride anions in the pit. Hence, if the chloride concentration of the solution is sufficiently high, then the salt cations remain in the pit and contribute with their corresponding chloride anions. Ernst and Newman concluded that the invariance of the CPT up to a certain chloride concentration is ascribed to the need for a salt film for initiation of natural pits and above the critical concentration natural pits initiate without a salt film [6].

Prosek et al calculated the solubility of different salts in water [8]. The solubility in water for magnesium chloride and sodium chloride was similar over a temperature interval of 10-80°C whereas calcium chloride was not comparable. These calculations indicate that the use of magnesium chloride as a salt in CPT measurement would be more suitable than the use of a salt of calcium chloride. The authors explain that the calcium chloride salt develops different phases which will stabilize with increasing temperature, i.e., $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$ (α), and $CaCl_2 \cdot 2H_2O$. However, it is also important to avoid saturated salt concentrations since the osmotic coefficient is indeed very different for sodium- calcium and magnesium chloride respectively [8].

Precipitations from solutions of $MgCl_2$ would possibly be hydroxides as $Mg(OH)_2$. In order to avoid these precipitations the pH in the $MgCl_2$ solution has to be below a certain value. Calculations by using the solubility product of $7.1\ 10^{-12}$ (20°C) results in pH values for precipitation between 8.2 for 3M $MgCl_2$ and 8.4 for 1M $MgCl_2$ [9].

2 Experimental

The CPT values of austenitic and duplex stainless steels were electrochemically measured in 1M NaCl and in 3M $MgCl_2$ solutions. Ranking of the CPT values of the stainless steels was carried out. The chloride amounts in the two different salt solutions were determined.

2.1 Materials

Stainless steel grades were chosen in order to receive CPT over a large temperature range.
The Pitting Resistance Equivalent, PRE, was calculated on the basis of the composition of the alloy, given in wt-%, and presents rough information on the pitting corrosion resistance of a stainless steel grade, according to:

PRE = %Cr + 3.3%Mo + 16%N

The equation relies on the important alloy elements for corrosion and a higher PRE value indicates a better resistance against pitting corrosion. Table 1 presents the grades, nominal composition and the PRE value of tested stainless steels.

Table 1: Nominal composition in wt-% of stainless steels tested and their PRE-value.

UNS	EN	Alloy	Micro-structure	PRE	Cr	Ni	Mo	C	Others
S31600	1.4401	316/316L	Austenite	26	17	10	2.1	≤0.03	
N90804	1.4539	904L	Austenite	35	20	25	4.5	≤0.025	Cu
S31254	1.4547	254SMO	Austenite	44	20	18	6.1	0.010	
S34565	1.4565	Sandvik 3REM69	Austenite	47	24	18	4.6	0.017	
S32654	1.4652	654 SMO	Austenite	57	24	22	7.3	0.010	
S32304	1.4362	Sandvik SAF 2304®	Duplex	25	22.5	4.5	0.3	0.03	
S32205	1.4462	Sandvik SAF 2205®	Duplex	35	22	5	3.2	0.03	
S32750	1.4410	Sandvik SAF 2507®	Duplex	43	25	7	4	≤0.03	

Triplicate specimens of the eight different steel grades included in this investigation were prepared as coupons in the size of 50×25×3 (mm). Any oxides remaining from production were removed either by pickling or by grinding the specimens with a stone surface prior to the normal grinding procedure. The coupons, including the cut ends were then ground with a P600 grit paper to receive reproducible surfaces. Finally the samples were degreased in acetone, brushed with a nylon brush and rinsed with ethanol prior testing.

2.2 Methods

The Critical Pitting Temperatures, CPT, were determined as prescribed in ASTM G 150 in 1M NaCl solution at a constant potential of +734mV vs the Ag,AgCl electrode (3.0 M KCl). The specimens were fully immersed in the solution during the measurements. The temperature of the solution was increased by a rate of 1 °C/min, starting from either 0 or 20°C, assuring that the CPT value was higher than 40°C for the higher starting temperature. The CPT was determined as the temperature when the current density exceeded 100 $\mu A/cm^2$ for a minimum of 60 s [9]. In the same way as described above, CPT_{mod} was determined in a solution of 3M $MgCl_2$.

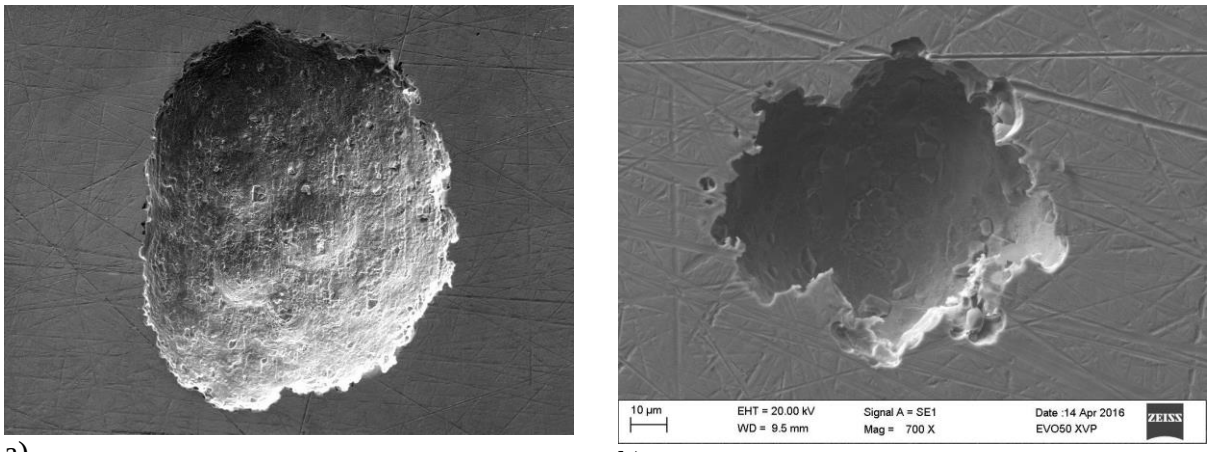
In order to verify any independence in the measured CPT with increasing chloride content, measurements were carried out on one steel grade, SAF 2205, at various concentrations between 1M and 5.4M of NaCl. The CPT was in addition measured in 0.5M $MgCl_2$, which was expected to correspond to the chloride concentration in 1M NaCl.

The pH was measured in the solutions with various chloride concentrations. The pH was measured using a pH meter, before and after some of the measurements. The chloride concentration was measured by potentiostatic titration, as well as by ion chromatography. Pitting was observed visually. For one of the samples, SAF 2507, pitting was demonstrated by Scanning Electron Microscopy, SEM.

3 Results

3.1 Critical Pitting Temperature

Pitting corrosion was obtained after corrosion tests following the procedure in ASTM G150 on the surfaces measured in both 1M NaCl and 3M $MgCl_2$. Figure 1 presents SEM images of measurements on SAF 2507 in the solutions.



a) b)

Figure 1. SEM images of pitting corrosion on Sandvik SAF 2507 after measurements in a) 3M $MgCl_2$ and b) in 1M NaCl . Images were recorded at 130 X and 700 X magnification , respectively.

Table 2 summarizes the mean values of CPT in 1M NaCl and CPT_{mod} in 3M $MgCl_2$ for the eight different steel grades, respectively. The PRE values are presented in the table. The higher the PRE, the higher pitting resistance is expected.

The CPT values measured in 1M NaCl solution all have values around 11±4 °C higher than in the $MgCl_2$ solution.

The steel grade 654 SMO does not give a CPT value in 1M NaCl solution, as the solution combined with the upper temperature limit of 100 °C, is not aggressive enough for such high alloyed grade. However, by using $MgCl_2$ solution in the modified method, a CPT_{mod} = 112 °C for this grade was determined.

Two of the grades, 316 and 254SMO showed pitting attacks on the edges, rather than on the surfaces. This gave slightly lower CPT values than expected from the steel grades.

Table 2: Temperatures in °C for pitting to occur in 1M NaCl (=CPT) and corresponding temperature in 3M $MgCl_2$. PRE, calculated for nominal composition of each alloy.

Alloy	CPT (°C), 1M NaCl	CPT_{mod} (°C), 3M $MgCl_2$	PRE
316L	20.3	9.0	26
Sandvik SAF 2304®	22.6	15.4	25
904L	47.7	32.5	35
Sandvik SAF 2205®	50.0	45.6	35
254 SMO	72.8 (edge corrosion)	64.7	43
Sandvik SAF 2507®	84.9	71.6	43
3REM69	94.7	79.3	47
654 SMO	-	111.6	57

Figure 2 shows the measured mean values of CPT in the two electrolytes as a dependence of pitting resistance, PRE value.

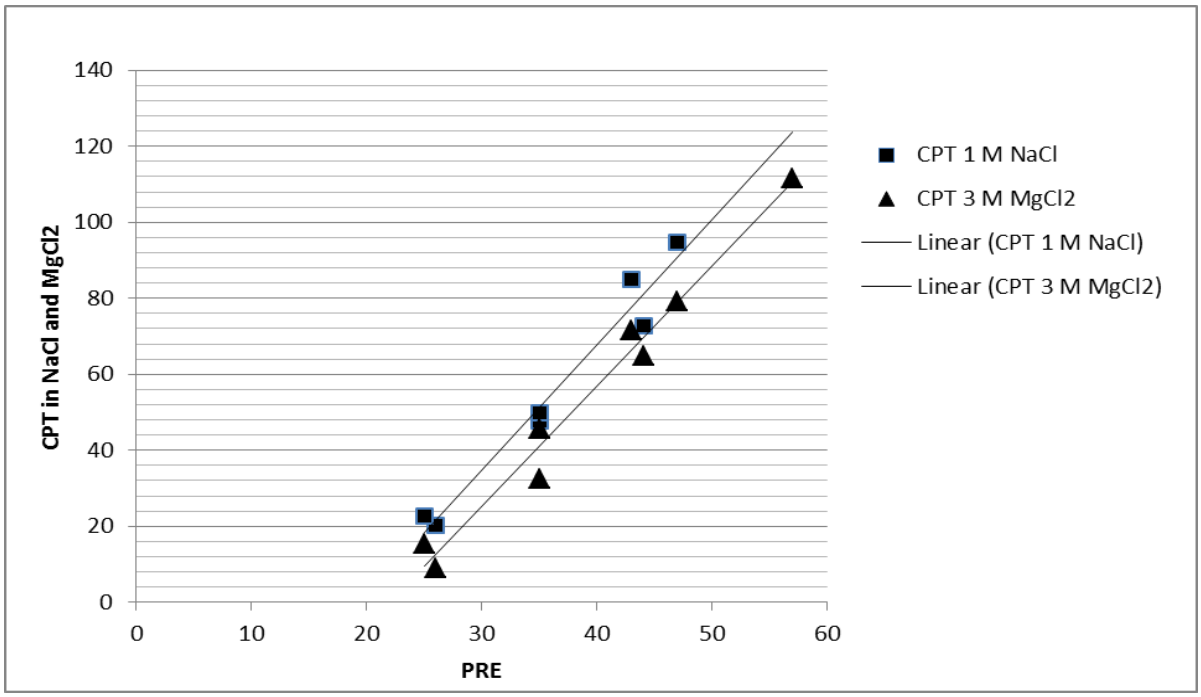


Figure 2. Measured CPT in 1M NaCl and 3M $MgCl_2$ as a dependence of PRE value.

The pH was 6.1-6.8 in the 1M NaCl solution and 4.1-5.3 in the 3M $MgCl_2$ solution. The pH values before and after CPT_{mod} measurements were the same. The pH is expected to be lower in the $MgCl_2$ solution as the Mg^{2+} ion is a stronger Lewis acid than the relatively neutral Na^{+}-ion and this is also observed in the pH measurements.

3.2 Chloride concentration dependence

The chloride concentration was measured by potentiostatic titration, as well as by ion chromatography (IC). Table 3 illustrates the results from both these methods. The results agree relatively well between the different methods.

Table 3: Chloride concentrations before and after CPT measurements, determined by potentiostatic titration and ion chromatography (IC).

Method	**Pot. titration**		**IC**	
	[Cl^-] before meas. (g/L)	[Cl^-] after meas. (g/L)	[Cl^-] before meas. (g/L)	[Cl^-] after meas. (g/L)
1M NaCl	36	36	33	33
1M NaCl	36	-	37	-
3M $MgCl_2$	226	223	216	230
3M $MgCl_2$	219	220	201	202

The chloride concentration is six times larger in the 3M $MgCl_2$ solution compared with the 1M NaCl solution which is in agreement with the stoichiometry of the solutions.

In order to evaluate the chloride concentration dependence, where the pH would not be expected to vary, CPT was measured in five different concentrations of NaCl solution, i.e. 1, 2, 3, 4 and 5.4M NaCl solution. To compare CPT values obtained in equal Cl^- concentration, CPT was measured in 1M NaCl and 0.5M $MgCl_2$ solutions, respectively. Table 4 summarizes the results from CPT measurements performed and shows the pH measured before measurements in each solution.

Strangely enough, the pH varies in the NaCl solution, but was probably approximately the same as the distilled water used when preparing the solutions. However, it can be concluded that the pH was 1-2 pH units lower in the 3M $MgCl_2$ solution compared to the NaCl solutions, as visualized in Table 4. The pH seems further to be affected by the amount of magnesium ions in the two different $MgCl_2$ solutions, the higher the concentration, the lower the pH, as would also be expected.

Table 4. CPT measurements for one steel grade, SAF 2205 but with different concentrations of NaCl and $MgCl_2$. The pH measured before the measurements is shown.

Concentration	**CPT (°C)** Average value	**pH**
1M NaCl	50.0	6.16
2M NaCl	50.1	7.80
3M NaCl	47.2	7.20
4M NaCl	47.7	6.40
5.4M NaCl	46.6	7.83
0.5M $MgCl_2$	50.1	6.45
3M $MgCl_2$	45.6	5.15

Figure 3 shows the dependence in both CPT and CPT_{mod} vs the chloride concentration in the different salts independent of the cation.

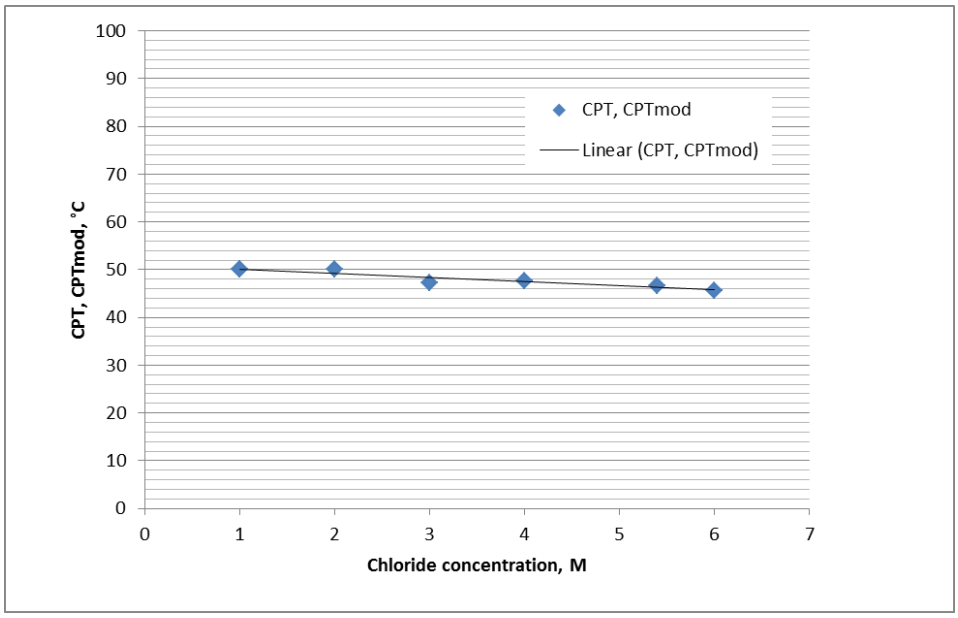


Figure 3. Measured CPT as a dependence of chloride concentration in the test solution, independent of cation.

The results show that the dependence of the chloride concentrations on CPT seems to be low, but at higher concentrations, *i.e.* 5.4M NaCl and 3M $MgCl_2$, the CPTs are slightly lower than in 1M NaCl. A standard deviation can be expected within the method of measuring CPT. However; the slightly lower CPT value for the 3M $MgCl_2$ solution may be influenced both by the very high chloride concentration and by the lower pH value.

4 Discussion

The method presented in this paper makes it possible to rank alloys with high PRE values, and gives reasonable linearity to the standard ASTM G150 method, as shown in Figure 2. By the use of $MgCl_2$ solution in CPT measurements, a higher boiling point is achieved and the CPT_{mod} could be given for alloys, where the use of NaCl as the electrolyte fails due to boiling of the solution. It is, however, not possible to correlate the two methods directly, the measurements are restricted to be a ranking method in either of the salt solutions.

The use of magnesium chloride has been criticised for measuring stress corrosion cracking, SCC, in stainless steels. However, in SCC measurements, very high concentrations of the salt are used and in the dilute $MgCl_2$ solutions used in this investigation, the salt behaves very similar to NaCl in terms of e.g. solubility. Therefore, magnesium chloride seems to be a suitable choice for the purpose.

The results from measurements in different chloride concentrations on Sandvik SAF 2205, indicate that up to a certain level, the increase in chloride concentration will not give a linear response in the lowering of CPT for higher chloride concentrations, but a comparable minor deviation in the CPT. However, measurements in chloride concentrations equal to or higher than 6M seems to result in lowering the CPT. This indicates that the difference of around 10-15°C in lower CPT for the 6M $MgCl_2$ solution can be mainly attributed to the combination of a higher chloride concentration and a lower pH in the solution.
One explanation to the differences in the CPT results measured in NaCl and $MgCl_2$ can possibly be found in the effect of the cation on metastable and propagating pitting corrosion.

The Mg^{2+}-ion is a stronger Lewis acid than the neutral Na^{+}-ion, which means that the solution containing Mg^{2+}-ions is expected to have a lower pH as compared to the NaCl solution. The effect of pH on the CPT value was previously reported in the literature where a lower CPT in 0.5M $MgCl_2$ was observed compared to 1M NaCl. A similar CPT was, however, revealed at the same pH when comparing 2M of chlorides from NaCl with 2M chlorides from $MgCl_2$. In addition, the CPT decreased as pH decreased and the conclusion was a change of CPT of around 10-20°C depending on steel grade and differences in pH [10]. These results do not show clearly that the magnesium cation is completely responsible for the lower pH and the lower CPT but that a lower CPT can be expected in a solution with lower pH.

The increase of the boiling point in higher concentrations, about 3M, of $MgCl_2$ provided an opportunity to use the ASTM G150 at elevated temperatures above the boiling point of NaCl. The concentration of 3M in $MgCl_2$ was thus chosen in order to increase the ability to use the methodology of ASTM G150 at higher temperatures. If all the chloride ions in the 3M $MgCl_2$ are expected to go into solution, the chloride concentration would be six times higher in the $MgCl_2$ solution than in the 1M NaCl solution. The results from chemical analysis seem to verify that this is also the case for a 3M solution and suggest that the solution is below the saturation of the salt. However, it cannot be excluded that there is an influence on the passive film from the $MgCl_2$-salt. A limit in concentration should therefore be a future concern in order to set a standard methodology. Conclusively, one important task to consider in designing the experimental parameters for ranking highly alloyed stainless steels in another salt than 1M NaCl, is to have the salt fully dissolved into solution as free chloride ions, and to avoid the saturation of the salt.

The chloride concentration was measured by potentiostatic titration, as well as by ion chromatography. The titration method is more reliable for the purpose of these measurements, because with such high concentrations as 1-6M chloride solutions, the solutions have to be diluted up to 100 000 times before measuring by ion chromatography. Moreover, ion chromatography results give the total chloride concentration, i.e. including complex ions, which will not take part in the pitting mechanism.

5 Conclusions

- CPT values measured by the standardized method, i.e. in 1M NaCl solution, were as expected. In 3M $MgCl_2$ solution, CPT_{mod} values up to 112 °C could be measured, and thereby broadening the range for where critical pitting temperatures can be obtained.
- The results for CPT_{mod} in 3M $MgCl_2$ showed sufficient linearity comparable with the linearity for CPT in 1 NaCl, but at values typically 11±4 °C lower.
- The modified method can successfully be used as a ranking method for very high alloyed materials, where the measurements in 1M NaCl are limited by the boiling point of the solution.
- It is not possible to rank materials by comparing measurements in different solutions; the measurements are restricted to be a ranking method in the same solution.
- The lowering of the CPT in $MgCl_2$ seems to result from the combination of higher chloride concentration and lower pH.

6 Acknowledgements

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