

Comparison of CPT-values of UNS N08935, UNS N06625, UNS N06455 and UNS N06985 by Use of a New Electrochemical Method

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ABSTRACT

The comparison of the pitting resistance of alloys with high corrosion resistance can be challenging, as CPT-values (critical pitting temperatures) are often above the boiling point of the test solutions. For high-nickel alloys, the use of potentiostatic electrochemical methods at increasing temperatures can also be questionable, as this alloy type often shows high or continuously increasing current densities with increasing temperature, rather than the desired distinct current peak at pitting. The applied electrochemical potential must also be proven to be below the transpassive potentials of the tested alloys.

A new electrochemical method has been developed in which CPT-values could be determined of alloys UNS N08935, UNS N06625, UNS N06455 and UNS N06985. The electrochemical potential used is shown to be below transpassive potentials. The current density versus temperature curves were analyzed and showed low passive current densities up to temperatures where pitting started.

CPT-values of the tested alloys were around 90°C for UNS N08935, UNS N06625 and UNS N06455 and 55°C for UNS N06985.

Key words: Pitting, Electrochemical, Transpassivity, MgCl_2 , Acidity, Chloride Concentration, UNS N08935, UNS N06625, UNS N06455, UNS N06985

INTRODUCTION

Laboratory CPT-tests often have the benefit of being quick and easy to perform and can give important information of the pitting resistance of different alloys. Tests of pitting resistance are also frequently

used for delivery testing, as a reduction in the CPT-value can identify defects in the materials. In this case a pass or fail-test at one temperature is typically done, instead of determining a CPT-value.

Additionally, CPT-values can be used to differentiate between the pitting resistance of different alloys. This can be valuable at materials selection and may assist in evaluating life-time cost related to properties. The actual conditions at the place of intended use must be well known, as for instance the pH-value or contaminants may influence the corrosion resistance.

Comparing CPT-values of different alloys

Some problems may be encountered when attempting to determine CPT-values for certain alloys or using specific methods. It may, for instance, be difficult to find CPT-values for alloys with very high pitting resistance, as pitting may initiate only above the boiling points of test solutions. ASTM⁽¹⁾ G48 was developed using a maximum temperature of 85°C.¹ Changed test conditions at increased temperatures have been reported, especially of the pH-value, the potential and formation of deposits on sample surfaces.^{2,3,4} Another standardized method, ASTM⁽¹⁾ G150, uses an applied electrochemical potential of 700 mV_{SCE} (SCE: saturated calomel electrode) and a critical current density for CPT of 0.1 mA/cm².⁵ It has the advantage of being quick, as CPT is determined without iterative procedure and each test typically has a duration of a few hours. On the other hand, the test was developed for stainless steels and its use for nickel alloys is questionable, primarily due to their often lower transpassive potentials and potentially higher passive current densities. The 1M NaCl-solution used in ASTM⁽¹⁾ G150 is also too weak for highly pitting resistant alloys to obtain pitting.

Although temperatures above 85°C might be questionable in the ASTM⁽¹⁾ G48-test, CPT-values at 100°C and higher have been reported.^{6,7} For the alloys included in this work, CPT-values from tests in acidified ferric chloride have been reported as shown in Table 1.^{2,6,8,9}

Table 1
CPT-values from ASTM⁽¹⁾ G48-tests

Alloy	CPT	Test Method and Comments
UNS N08935	>85°C	C Not tested >85°C
UNS N06455	100°C	C
UNS N06625	>85°C	C
UNS N06985	77°C	E*

*Note that test method E has a shorter testing time of 24 hours versus 72 hours for method C.

If restricting the ASTM⁽¹⁾ G48-test to a maximum temperature of 85°C, as per the reported warnings, only one of the four alloys, UNS N06985, can be separated from the others based on its CPT-value from this test.

Another relatively common, albeit not standardized, method for CPT-determination is testing in the so-called Green Death-solution. The procedure may vary, such as testing time and solution recipe, potentially leading to difficulties when attempting to compare results from different tests. CPT-values in the Green Death-solution have been determined in this work to enable a comparison to CPT-values from the new method.

Input for the development of a new CPT-method

Previous work to determine CCT-values (critical crevice corrosion temperatures) using a modified version of the ASTM⁽¹⁾ G150-standard showed that the otherwise high and sometimes increasing passive currents of UNS N06625, decreased at decreased pH-values.¹⁰ A reduced pH-value has also

been reported to increase the transpassive potential (E_{TP}) in chloride solutions.¹¹ On the other hand, a too low pH-value, where general corrosion could start to dominate over pitting, should be avoided.

During the verification of a modified version of ASTM⁽¹⁾ G150, where 3M $MgCl_2$ was used, potential independent CPT-values of stainless steels were obtained not only at 700 mV_{SCE}, but also at 600 mV_{SCE}.¹²

It has been shown that CPT-values of stainless steels decrease with increasing chloride concentration.^{13,14} It was therefore presumed that CPT-values could be reduced by increasing the chloride concentration. The CPT-value of UNS N08935 has for instance been difficult to determine in 3M $MgCl_2$, as pit initiation occurred at or above the boiling point.

The aim of this work has been to enable a comparison of CPT-values of highly pitting resistant alloys by use of a suitable modification of the ASTM⁽¹⁾ G150-method.⁵

EXPERIMENTAL PROCEDURE

Material

Flat samples of alloy Sandvik Sanicro® 35[†] (UNS N08935) were taken from tubes and samples from the other alloys were taken from plate material. Due to different sizes of the original material, all samples were 50x20x4 mm, except for samples of UNS N06625 where test-pieces were 30x25x4.3 mm. For the electrochemical CPT-tests, four samples were used for UNS N08935, UNS N06455 and UNS N06985 and two samples of UNS N06625. Four to six samples per alloy were needed to determine CPT in the Green Death-method. All samples had Ø 5 mm holes for hanging on platinum hooks in electrochemical tests. Alloying elements of interest for comparison, including those used in common PRE-values (pitting resistance equivalent), are listed in Table 2.

Table 2
Nominal chemical composition (w-%) of alloys tested (selected elements).

UNS-No	Fe	Cr	Mo	Ni	N	W
N08935	Bal.	27	6.5	35	0.3	<0.001
N06625	≤5	21	9	62	0	0
N06455	≤3	16	16	65	0	0
N06985	Bal.	22	7	50	0	1

Before electrochemical tests, the samples were ground to 600 grit on all surfaces, including softening of sharp edges. Grinding to 120 grit was used before tests in Green Death-solution. After grinding, samples were stored for at least 24 hours in normal atmosphere to allow re-passivation. Before and after tests, samples were cleaned in water with a soft brush and degreased with acetone and ethanol and finally dried with compressed air.

Weight losses were recorded, and all samples were examined in a stereo microscope at 20X magnification or higher after all tests.

Electrochemical tests

The temperature control, at a set temperature or at a temperature increase of 1°C/minute, was done via a control system of the potentiostat. This was connected to a heater which circulated silicon oil to a double walled glass cell. Pt100-sensors in the test solution monitored the solution temperature and were also connected to the control unit to regulate the temperature or temperature increase.

Solutions were purged with nitrogen gas throughout the measurements. Ag/AgCl with 3M KCl was used as a reference electrode and a platinum net as a counter electrode. Samples were hung on platinum hooks to enable electrical contact.

CPT-measurements in 4.5 M MgCl₂ – new method

A solution of 4.5M MgCl₂ with a pH-value adjusted to pH=5 by addition of small amounts of NaOH was used.

The ASTM⁽¹⁾ G150-standard was mimicked by using the following parameters.⁵

- Initial measurement of OCP (Open Circuit Potential)
- A temperature-increase of 1°C/minute
- A critical current density of 0.1 mA/cm²

Complementary parameters:

- The OCP-measurement was done for one hour before the potential was increased
- A scan rate of 10 mV/second was used to increase the electrochemical potential from the OCP. For the purpose of this work, this scan was recorded.
- An electrochemical potential of 600 mV_{SCE} (634 mV vs Ag/AgCl) was used.
- The starting temperature was 20°C, according to ISO⁽²⁾ 17864, as CPT-values >40°C were expected for all four alloys.¹⁵

Besides using the resulting curves to determine CPT-values, i.e. current densities a function of temperature, they were also analyzed with respect to the current development at the potential increase, the passive current density (below CPT) and the increase of the current density between CPT-1°C and CPT.

Potentiodynamic scans

Potentiodynamic scans were made to verify that the chosen potential of 600 mV_{SCE} was below the transpassive potentials of the tested alloys. As it has been reported that transpassive potentials can decrease with increasing temperatures, curves were recorded at elevated temperatures.¹⁶ As pitting was not desired in this case, temperatures 20°C below the previously determined CPT-values were used (T=CPT-20°C). A scan rate of 10 mV/s was chosen from OCP to 634 mV (Ag/AgCl) to avoid very high currents in this potential range. Some experiments using other scan rates, such as 10 mV/minute, gave continuously increasing currents at low potentials, which rendered E_{TP}-determinations impossible. The higher scan rate was therefore used up to 600 mV_{SCE}, where after the more common scan rate of 10 mV/minute was used.¹⁷

Tests in Green Death-solution

The test was performed using a 72-hour testing-time, a temperature step of 5°C, new samples at each temperature and a solution consisting of 11.5 w% H₂SO₄, 1.2 w% HCl and 1 w% each of FeCl₃ and CuCl₂. Weight losses were recorded, and microscopy was done to evaluate if pitting had occurred.

RESULTS

CPT-measurements in 4.5M MgCl₂

CPT-determination

CPT-values are given in Table 3. Typical curves, temperature vs. current density, are shown in Figure 1.