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Development of "Unified" Methodology Examining the Critical Pitting/Repassivation Potential and Temperature

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ABSTRACT

Standards ASTM G61 - used for Cyclic Potentiodynamic Polarization measurements, and G150 - used in Critical Pitting Temperature measurements, are commonly used to determine the susceptibility of corrosion resistant alloys to localized corrosion. The two methodologies utilize different, yet related, driving forces applicable to the process, namely the potential and temperature. This study sought to establish the relationship between the pitting potential from ASTM G61 and critical pitting temperature from ASTM G150, both of which are determined as the driving force, potential or temperature, is on the increase. ASTM G61 also establishes the repassivation potential as the potential is decreased. In this study, ASTM G150 is extended to define the repassivation temperature for a decreasing temperature. The "unified" approach was utilized to identify the transition of a material from passive to active and its return to passive. Laboratory experiments were performed with UNS S32205 in a solution of sodium chloride.

Key words: UNS S32205, Pitting Potential, Pitting Temperature, Repassivation Potential, Repassivation Temperature

INTRODUCTION AND BACKGROUND

Cyclic potentiodynamic polarization, as defined in ASTM G 61, and temperature-dynamic polarization, as defined in ASTM G 150, have been utilized to assess the localized corrosion susceptibility of CRA.^{1,2} In both test procedures, the onset of pitting is determined by the abrupt increase in the current response at the onset of localized corrosion of the system. Repassivation being defined as the return of the current response to the passive condition.

In this study an attempt has been made to “unify” these two separate test protocols and present the results from each on a common basis. This would allow data generated from the two methods to be compared in a consistent manner to further improve materials selection decisions.

The two key ASTM standards for determining the susceptibility of alloyed materials are ASTM G 61 and ASTM G 150, each of which is briefly described in the following.^{1,2,3,4,5,6}

ASTM G 61

ASTM G 61 describes the test method for conducting cyclic potentiodynamic polarization curves to determine localized corrosion parameters such as the pitting potential, E_P , and the repassivation potential, E_{RP} . The methodology in G 61 is summarized below,

- Wet-grind the specimen surface to 600-grit SiC paper and degrease
- Purge the solution for approximately 1 hour with inert gas to remove oxygen
- Immerse the specimen in a temperature-controlled solution for 1 hour prior to polarization
- Start the potential scan from the corrosion potential, E_{Corr}
- Scan in the noble direction at 0.6 V h^{-1} (10 mV min^{-1})
- The onset of localized corrosion is indicated by an inflection in the current response
- Reverse the potential scan when the current exceeds 5 mA cm^{-2}
- Continue the reverse scan until the hysteresis loop closes or the corrosion potential is reached
- The polarization scan data plotted with the potential as the ordinate and $\log_{10}$ of the absolute value of the current on the abscissa

It should be noted that while the final output is plotted as E-log i the data is actually recorded as two time-series, E versus t and i versus t. The measurement process and key localized corrosion parameters are illustrated in Figure 1.

ASTM G 61 Adaptation

In order to make the results comparable between the two ASTM standards the ASTM G 61 procedure was modified such that the current criteria for defining E_P and E_{RP} was defined to be the same as that of ASTM G 150 i.e. $100 \mu\text{A cm}^{-2}$, when the current crosses from low-to-high defining E_P and high-to-low defining E_{RP} .

The ASTM G 150 current criteria was chosen to give a clear, consistent and unequivocal current criterion in all tests, namely $100 \mu\text{A cm}^{-2}$.

ASTM G 150

ASTM G 150 describes the test method for electrochemical determination of the critical pitting temperature, CPT. The methodology is summarized below,

- Clean and immerse the specimen in the solution and record the open circuit potential
- Allow the system to stabilize at the starting temperature for a minimum of 10 minutes
- Apply the constant anodic potential for 20 s prior to starting the temperature ramp
- Ramp the temperature at 1°C min^{-1} until the CPT current criteria of $100 \mu\text{A cm}^{-2}$ is exceeded

As with ASTM G 61 the temperature and current are recorded as time series and is illustrated in Figure 2.

ASTM G 150 Adaptation

For this work the ASTM G 150 procedure was extended to include a temperature ramp down in order to obtain the repassivation temperature (RPT), and as illustrated in Figure 2 defined with the same current criteria as the CPT, i.e. $100 \mu\text{A cm}^{-2}$.^{8,9,10,11,12} The temperature ramp-down rate of change on the cooling part of the cycle was the same as the heating cycle, namely 1°C min^{-1} . Additionally, ASTM G 150 recommends holding a potential of 700 mV, as a result for this work a range of potential values other than 700 mV vs SCE were used.

APPROACH TO UNIFICATION

The ASTM standards can be summarized as,

- ASTM G 61, CPP, is a constant temperature varying potential method - ramp-up followed by a ramp-down to determine the on-set of pitting, E_P , and repassivation, E_{RP}
- Extended ASTM G 150, CPT, is a constant potential varying temperature method - ramp-up followed by a ramp-down to determine the on-set of pitting, CPT, and repassivation, RPT
- Both methods utilize an inflection or abrupt change in the current response to indicate the on-set of localized corrosion although the absolute definitions are slightly different,
 - ASTM G 61 the inflexion point in the current response
 - ASTM G 150 the $100 \mu\text{A cm}^{-2}$ current criteria

In principle then both methods can be combined to define a temperature-potential domain¹¹ delineated by an upper bound of E_P and CPT, and a lower bound of E_{RP} and RPT, and illustrated in Figure 3. For the purposes of this work, the current limit of $100 \mu\text{A cm}^{-2}$ was used in both CPP and CPT tests.

EXPERIMENTAL PROCEDURE

The test solution, NaCl, was 30,000 ppm_w of Cl⁻ or 0.85 M. The brine solutions were prepared with reagent grade chemicals and deionized (DI) water. During testing, the solution was saturated and continually purged with reagent grade CO₂.

Tests were performed using a flooded gasket electrochemical cell as described in detail in Qvarfort.⁷ The temperature of the cell was controlled by a heat exchanger with a temperature controlled polytetrafluoroethylene (PTFE) coated copper coil. The flat specimen had an exposure surface area of 5 cm² and was mounted under the flooded gasket. Ports by the specimen were available for the gasket flush water supply, and the reference electrode Luggin capillary. The Luggin capillary extended outside the test cell itself keeping the reference electrode at ambient temperature approximately 25 °C.

CPP measurements were collected with a commercial computer controlled-potentiostat. The testing followed the guidelines provided in ASTM G61.¹ The specimen was polarized from -100 mV vs. OCP to +1200 mV vs. Ag/AgCl at a scan rate of 10 mV min⁻¹. The scan was reversed at the upper potential or if the current threshold 1 mA cm⁻² was reached. The current threshold used was less than the ASTM G61 recommended value of 5 mA cm⁻² in order to prevent excessive contamination of the solution with corrosion product ions.

The current and potential sampling frequency was 1 Hz with all potentials measured with respect to an Ag/AgCl reference electrode. The CPP tests were performed at a constant temperature of 60 °C and 70 °C.

Potentiostatic CPT tests were performed to study the pitting behavior of UNS S32205 following the guidelines provided by ASTM G150 with adaptations list above, namely a cooling ramp and a range of potentials.² Experiments were performed with the same electrochemical cell and specimen configuration described above. The potential was controlled with a commercial computer controlled-potentiostat. The temperature was ramped from room temperature to 80 °C at a rate of 1 °C min⁻¹. The upper temperature limit of 80 °C was selected in order to prevent excessive evaporation of the solution.

The specimens were prepared from UNS S32205⁽¹⁾ and ground to 600-grit SiC before being degreased. The composition of UNS S32205 plate is given in Table 1.

Table 1
Composition of UNS S32205 Plate Used for Specimen Preparation

Cr	Ni	Mn	Si	P	S	C	N	Mo	Fe
22.62%	5.58%	1.27%	0.43%	0.025%	0.001%	0.025%	0.18%	3.05	Bal.

⁽¹⁾ A detailed micrographic structural determination was not performed

RESULTS AND DISCUSSION

The experimental conditions and results from the CPP and CPT tests are summarized in Table 2. The potential and temperature conditions were selected based on prior experience with this alloy where it was known localized corrosion would occur. This was a compromise between the range of test conditions and the requirement to establish both a pitting condition and repassivation condition in each test. The detailed time series for each complete test are presented in Figure 4 through Figure 6 as well as the current criteria of $100 \mu\text{A cm}^{-2}$ for determining pitting and repassivation potential and temperatures.

As this test program was only designed to test the “proof-of-concept” only single test for each set of conditions were conducted. In order to develop the approach further replicate tests would be required to demonstrate reproducibility.

Table 2
Summary of the experimental conditions and the results from the CPP (ASTM G 61) and CPT (ASTM G 150) test program – all potentials are measured with respect to Ag/AgCl at test conditions

Type	Test	Conditions	Pitting E_P or CPT	Repassivation E_{RP} or RPT
CPP	1	60 °C	542 mV	182 mV
	2	70 °C	324 mV	64 mV
CPT	3	450 mV	59 °C	29 °C
	4 ⁽²⁾	350 mV	69 °C	-

As noted earlier both ASTM G 61 and ASTM G 150 determine a critical temperature and potential at which $100 \mu\text{A cm}^{-2}$ is exceeded, in case of the on-set of localized corrosion, pitting, and returned-to in the case of repassivation. After Hornus et. al., the temperature and potential determined in each test for pitting and repassivation can be combined onto a single curve and are shown in Figure 7 with the upper boundary determined using the CPP and CPT data, and the lower boundary defined by E_{RP} and RPT.¹²

Figure 7 clearly shows the equivalence of the two methods and demonstrates that results from the two methods can be presented on a common basis.

⁽²⁾ Power/instrumentation issues resulted in the partial loss of data, as a result only the CPT could be established from surviving information