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ABSTRACT

In general, the susceptibility of Alloy 22 to suffer crevice corrosion is measured using the Cyclic Potentiodynamic Polarization (CPP) technique. This is a fast technique that gives rather accurate and reproducible values of repassivation potential (ER1) in most cases. In the fringes of susceptibility, when the environment is not highly aggressive, the values of repassivation potential using the CPP technique may not be highly reproducible, especially because the technique is fast and because many times the presence of transpassivity may hinder the nucleation and propagation of crevice corrosion. To circumvent this, the repassivation potential of Alloy 22 was measured using a slower method that combines Potentiodynamic-Galvanostatic-Potentiostatic steps (called here the Tsujikawa-Hisamatsu Electrochemical or THE method). The THE method applies the charge to the specimen in a more controlled way, which may give more reproducible repassivation potential values, especially when the environment is not aggressive. The values repassivation potential of Alloy 22 in sodium chloride plus potassium nitrate solutions was measured using the THE and CPP methods. For practical purposes, especially under the most aggressive conditions, both methods yield similar values of repassivation potential.

INTRODUCTION

Alloy 22 (N06022) is a nickel base alloy designed to be resistant to all forms of corrosion. Alloy 22 contains approximately 56% nickel (Ni), 22% chromium (Cr), 13% molybdenum (Mo), 3% tungsten (W) and 3% iron (Fe) (ASTM B 575). [1] Because of its high level of Cr, Alloy 22 remains passive in most industrial environments and therefore has an exceptionally low general corrosion rate. [2-6] The combined presence of Cr, Mo and W imparts Alloy 22 with high resistance to localized corrosion such as pitting corrosion and stress corrosion cracking even in hot high chloride (Cl^-) solutions. [7-12] It has been reported that Alloy 22 may suffer localized corrosion such as crevice corrosion when it is anodically polarized in chloride containing solutions. [8-10,13-15] It is also known that the presence of nitrate (NO_3^-) in the solution minimizes or eliminates the susceptibility of Alloy 22 to crevice corrosion. [8-10,16-23] The value of the ratio ($[NO_3^-]/([Cl^-]$) has a strong effect of the susceptibility of Alloy 22 to crevice corrosion. [16-25] The higher the nitrate to chloride ratio the stronger the inhibition by nitrate. This ratio may depend on other experimental variables such as total concentration of chloride or temperature. Other anions in solution were also reported to inhibit crevice corrosion in Alloy 22. [19-20, 26-28]

The susceptibility of Alloy 22 to suffer crevice corrosion is generally measured using the cyclic potentiodynamic polarization (CPP) technique, which is described in ASTM G 61 standard. [29] This is a fast technique that gives rather accurate and reproducible values of repassivation potential (ER1) in most cases. In the fringes of susceptibility, when the environment is not highly aggressive, the values of repassivation potential using the CPP technique may not be highly reproducible, especially because the technique is fast and because many times the presence of transpassivity may hinder the nucleation and propagation of crevice corrosion. To circumvent this, the repassivation potential of Alloy 22 was measured using a slower method that combines Potentiodynamic-Galvanostatic-Potentiostatic steps (called here the Tsujikawa-Hisamatsu Electrochemical or THE method). [15,30] The THE method applies the charge to the specimen in a more controlled way, which may give more reproducible repassivation potential values, especially when the environment is not aggressive.

EXPERIMENTAL TECHNIQUE

Alloy 22 specimens were mainly prepared from 1-inch thick plate. The specimens were creviced using a ceramic washer and PTFE tape. [15,30] There are two types of specimens, multiple crevice assemblies (MCA) [23] or lollipops and prism crevice assemblies (PCA). [15] All the tested specimens had a finished grinding of abrasive paper number 600 and were degreased in acetone and treated ultrasonically for 5 minutes in de-ionized (DI) water 1 hour prior to testing. Specimens were non-welded (MA) base plate or in the as-welded (ASW) condition. The weld was produced with matching filler metal using Gas Tungsten Arc Welding (GTAW). The welded specimens were not all weld metal but contained a weld seam which varied in width from approximately 8 to 15 mm.

Electrochemical tests were carried out in nine different NaCl and KNO_3 electrolytes. The following solutions were used: 1 m NaCl + 0.05 m KNO_3, 1 m NaCl + 0.15 m KNO_3, 1 m NaCl + 0.5 m KNO_3, 3.5 m NaCl + 0.175 m KNO_3, 3.5 m NaCl + 0.525 m KNO_3, 3.5 m NaCl + 1.75 m KNO_3, 6 m NaCl + 0.3 m KNO_3, 6 m NaCl + 0.9 m KNO_3 and 6 m NaCl + 3 m KNO_3. These solutions correspond to three molar ratios of nitrate over chloride: 0.05, 0.15 and 0.5. The testing temperatures were 60°C, 80°C and 100°C. The pH of the solutions was not adjusted and they were near neutral. Nitrogen (N_2) was purged through the solution at a flow rate of 100cc/min for 24 hours while the corrosion potential (E_{corr}) was monitored. Nitrogen bubbling was continued throughout all the electrochemical tests. The electrochemical tests were conducted in a one-liter, three-electrode, borosilicate glass flask (ASTM G 5). [29] A water-cooled condenser combined with a water trap was used to avoid evaporation of the solution and to prevent the ingress of air (oxygen). All the tests were carried out at ambient pressure. The reference electrode was saturated silver chloride (SSC) electrode, which at ambient temperature has a potential of 199 mV more positive than the standard hydrogen electrode (SHE). The reference electrode was connected to the solution through a water-jacketed Luggin probe so that the electrode was maintained at near ambient temperature. The counter electrode was a flag (36 cm^2) of platinum foil spot-welded to a platinum wire. All the potentials in this paper are reported in the SSC scale.

Cyclic Potentiodynamic Polarization - CPP: In these tests the potential scan was started 150 mV below E_{corr} at a set scan rate of 0.167 mV/s. The scan direction was generally reversed when the current density reached 5 mA/cm^2 in the forward scan. In a few tests the maximum applied potential was 600 mV. Depending on the range of applied potentials, each CPP test could last between 1 h and 3 h. This is a fast and efficient method to determine crevice corrosion resistance of commercial alloys. In the forward scan of the CPP, the potentials for which the current density is 20 and 200 $\mu A/cm^2$ are called E20 and E200. These parameters represent values of breakdown potentials (Figure 1). In the reverse scan of the CPP the values of potentials for which the current density is 10 and 1 μA/cm² are called ER10 and ER1. The potential at which the reverse scan intersects the forward scan is called repassivation potential cross over (ERCO) (Figure 1). ER10, ER1 and ERCO represent values of repassivation potentials.

The Tsujikawa-Hisamatsu Electrochemical test - THE: The second test used to assess the susceptibility of Alloy 22 to localized corrosion and passive stability was the Tsujikawa-Hisamatsu Electrochemical test, which currently does not have an approved ASTM standard. The potential scan was started 150 mV below E_{corr} at a set potentiodynamic scan rate of 0.167 mV/s. Once the current density reached a predetermined value (for example 20 μA/cm² or 2 μA/cm²), the controlling mode was switched from potentiodynamic to galvanostatic and the predetermined current density was usually applied for 2 h. The resulting potential at the end of the galvanostatic treatment was recorded. After the galvanostatic step, the treatment was switched to a potentiostatic mode. The potentiostatic steps were applied for 2 h starting at the potential recorded at the end of the galvanostatic treatment minus 10 mV and applying as many steps as necessary until crevice repassivation was achieved. Each subsequent potentiostatic step was 10 mV lower that the previous step. Generally 10 steps (or a total of 100 mV) were necessary to achieve repassivation of an active crevice-corrosion. The repassivation potential is determined as the potential for which the current density decreased as a function of time in the period of treatment of 2 h (Figure 2). Depending of the applied time and number of potentiostatic steps, each THE test could last between 24 h and 30 h. This is a lengthy test, which yields only one parameter, the crevice repassivation potential (ER, CREV). Determination of ER,CREV from the data may be subjective.

After the CPP and THE tests, the specimens were examined in an optical stereomicroscope at a magnification of 20 times to establish the mode and location of the attack.

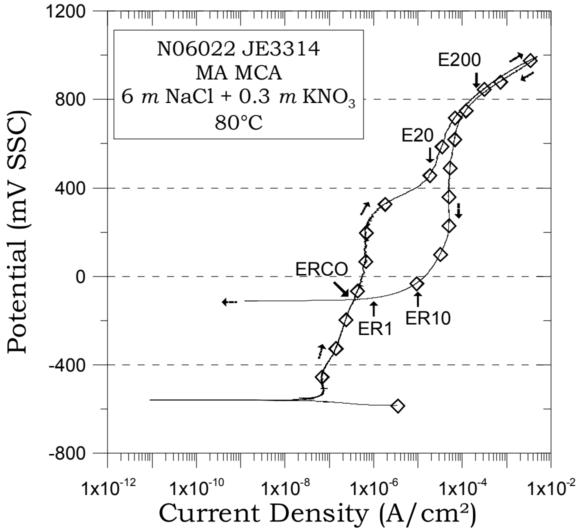

Figure 1 – Cyclic potentiodynamic polarization or CPP of specimen JE3314

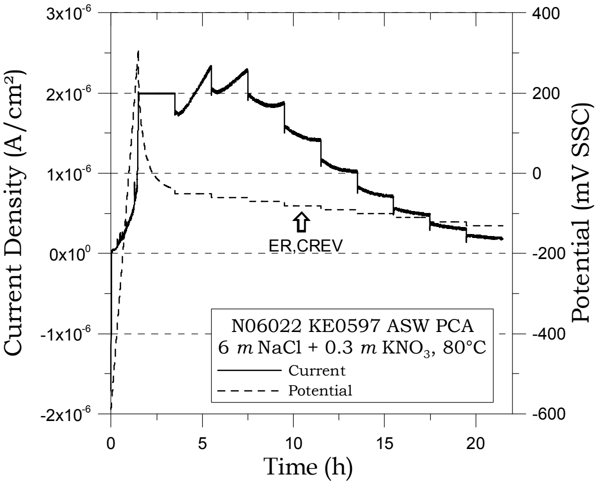

Figure 2 – Tsujikawa Hisamatsu Electrochemical or THE of specimen KE0597

REPASSIVATION POTENTIAL USING CPP and THE

Most of the results from the CPP tests were published before. [21,23] Figure 1 shows a typical cyclic potentiodynamic polarization curve for Alloy 22 and also the explanation of the parameters E20, ER1 and ERCO in Table 1.

Table 1 – Typical potentials from the CPP curves

Electrolyte	Temp. (°C)	E_{corr} 24-h ± SD	E20 ± SD	ER1 ± SD	ERCO ± SD	Mode of Attack
1 m NaCl + 0.05 m KNO_3	60	-408 ± 54	NA (>600)	258 ± 149	221 ± 180	No CC
	80	-411 ± 105	NA (>600)	34 ± 18	-14 ± 54	CC
	100	-539 ± 61	366 ± 61	-89 ± 20	-94 ± 25	CC
1 m NaCl + 0.15 m KNO_3	60	-326 ± 174	NA (>600)	424 ± 150	425 ± 174	No CC
	80	-455 ± 53	NA (>600)	305 ± 21	312 ± 30	No CC
	100	-509 ± 8	404 ± 0^A	-49 ± 0^A	-65 ± 0^A	CC-II
1 m NaCl + 0.5 m KNO_3	60	-397 ± 55	NA (>600)	436 ± 101	348 ± 0^A	No CC
	80	-438 ± 35	NA (>600)	329 ± 25	325 ± 27	No CC
	100	-529 ± 63	601 ± 13	306 ± 71	310 ± 79	No CC
3.5 m NaCl + 0.175 m KNO_3	60	-472 ± 53	659 ± 28	41 ± 88	-40 ± 47	CC-II
	80	-491 ± 10	477 ± 30	-54 ± 5	-81 ± 6	CC
	100	-506 ± 57	390 ± 0	-111 ± 13	-118 ± 20	CC
3.5 m NaCl + 0.525 m KNO_3	60	-381 ± 126	583 ± 16	360 ± 107	467 ± 220	No CC
	80	-433 ± 63	NA (>600)	410 ± 91	406 ± 119	No CC
	100	-417 ± 118	405 ± 47	-59 ± 29	-32 ± 88	CC
3.5 m NaCl + 1.75 m KNO_3	60	-375 ± 132	NA (>600)	429 ± 152	411 ± 154	No CC
	80	-480 ± 19	516 ± 0^A	321 ± 40	328 ± 53	No CC
	100	-491 ± 20	453 ± 0^A	312 ± 0^A	319 ± 0^A	No CC
6 m NaCl + 0.3 m KNO_3	60	-353 ± 259	NA (>600)	213 ± 220	177 ± 276	No CC
	80	-496 ± 19	451 ± 20	-80 ± 24	-103 ± 9	CC
	100	-474 ± 103	260 ± 29	-84 ± 18	-88 ± 19	CC
6 m NaCl + 0.9 m KNO_3	60	-326 ± 196	678 ± 0^A	442 ± 123	350 ± 0^A	No CC
	80	-485 ± 31	597 ± 67	127 ± 155	64 ± 167	CC-II
	100	-372 ± 206	495 ± 70	-60 ± 24	-73 ± 18	CC
6 m NaCl + 3 m KNO_3	60	-446 ± 59	731 ± 0^A	480 ± 156	346 ± 0^A	No CC
	80	-441 ± 71	719 ± 0^A	419 ± 159	285 ± 0^A	No CC
	100	-435 ± 110	473 ± 0^A	309 ± 0^A	299 ± 0^A	No CC
SD = Standard deviation, NA = Not Available (some of the polarization tests were conducted to maximum of 600 mV, ^{A} Single value. For CC and CC-II see Reference 21.						

Figure 3 shows the representation of the average ER1 from Table 1 as a function of the temperature for Alloy 22 in 3.5 m NaCl solution at two concentrations of NO_3^- to obtain ratios R = 0.05 and 0.5. For the higher nitrate content, the higher the repassivation potential ER1. As the temperature increases, ER1 decreases. Figure 1 also shows that as the system is more aggressive (higher temperatures and lower ratio R) the standard deviation decreases.

Table 2 shows the repassivation potentials ER,CREV obtained for Alloy 22 using the THE method. Fewer data are available since this method is more time consuming than the CPP method. Figure 2 shows a typical THE test result with a repassivation potential of -71 mV (Table 2). Figure 4 shows comparatively the repassivation potentials ER1 and ER,CREV obtained using CPP and THE, respectively. Figure 4 show that both tests yield similar repassivation potentials. When the system is not highly aggressive, for example at the lower temperatures, the repassivation potential using THE could be slightly lower than the repassivation potential using THE. However, for the most aggressive electrolytes the repassivation potential using both methods are practically undistinguishable from each other.

Comparing the results in Tables 1 and 2 it is apparent that using the CPP method crevice corrosion was clearly observed at the nitrate over chloride ratio of 0.05 at 80 and 100°C and at the ratio of 0.15 at 100°C (Table 1). At all the other six tested conditions the specimens suffered mostly transpassivity and Type II CC because the potential was driven to high values in a fast manner. Type II CC is slight and dull (non-crystalline). [21] Table 2 shows that using the THE test, crevice corrosion was also observed for the conditions reported in Table 1 plus at the nitrate over chloride ratio of 0.05 and 0.15 at 60°C and at the ratio of 0.15 at 80°C. Using the THE method, at the only nitrate over chloride ratio for which crevice corrosion was not observed was at 0.5, at all the tested temperatures.

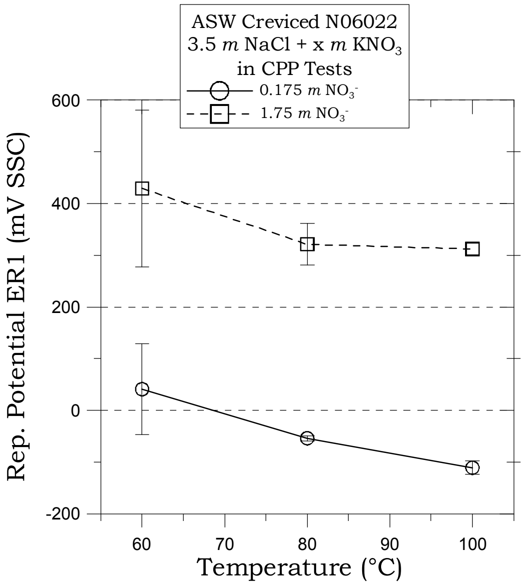

Figure 3 – ER1 for Alloy 22 as a function of temperature and nitrate concentration

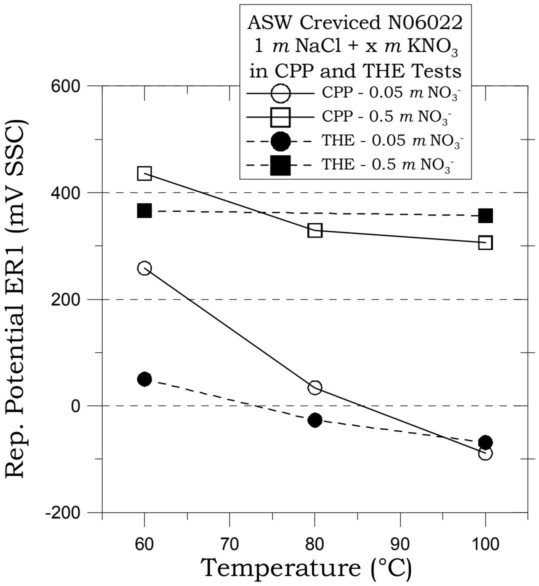

Figure 4 – Comparative repassivation potentials between CPP and THE methods

SUMMARY

1. Cyclic potentiodynamic polarization (CPP) curves are a fast method to determine the repassivation potential of Alloy 22
2. The Tsujikawa-Hisamatsu electrochemical (THE) method is more time consuming and it is designed to promote crevice corrosion in Alloy 22 without taking the alloy into transpassivity
3. For practical purpose, both the CPP and the THE methods yield similar values of repassivation potentials

Table 2 – Repassivation Potentials with the THE method

Electrolyte	Temp. (°C)	Specimen Designation	ER,CREV (mV SSC), THE	Mode of Attack
1 m NaCl + 0.05 m KNO_3	60	KE0176	49	CC
	60	KE0179	58	CC[A]
	60	KE0183	44	CC[B]
	80	KE0184	-27	CC
	100	KE0173	-69	CC
1 m NaCl + 0.15 m KNO_3	60	KE0628	264	CC
	80	KE0596	(<333)	CC
	80	KE0600	(>0)	CC[C]
	80	KE0624	19	CC
	100	KE0180	-22	CC
1 m NaCl + 0.5 m KNO_3	60	KE0119	366	No CC
	100	KE0752	(>357)	No CC
3.5 m NaCl + 0.175 m KNO_3	60	KE0177	20	CC
	80	KE0185	-42	CC
	100	KE0174	-93	CC
3.5 m NaCl + 0.525 m KNO_3	80	KE0629	3	CC
	100	KE0181	-55	CC
3.5 m NaCl + 1.75 m KNO_3	60	KE0120	340	No CC
	100	KE0753	330	CC
6 m NaCl + 0.3 m KNO_3	60	KE0178	2	CC
	80	KE0597	-71	CC
	100	KE0175	-103	CC
6 m NaCl + 0.9 m KNO_3	80	KE0630	-26	CC
	100	KE0182	-71	CC
6 m NaCl + 3 m KNO_3	60	KE0751	379	No CC
	100	KE0754	379	CC

CC = Crevice Corrosion. [A] Galvanostatic step at 1 µA/cm² for 2 h. [B] Galvanostatic step at 0.5 µA/cm² for 2 h. [C] Galvanostatic step at 1 µA/cm² for 8 h. Values in brackets = test terminated before repassivation potential was reached.

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