Effect of thermal treatment on the localized corrosion behaviour of alloy 718

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Summary

Nickel (Ni) based Alloy 718 (UNS N07718) is used extensively for Oil & Gas applications requiring yield strength levels in excess of 1000 MPa, mainly in the heat treated high strength condition for downhole and wellhead accessories and other components. It was of interest to determine how age hardening heat treatments affect the corrosion behavior of N07718. Alloy 718 was tested in the as-received condition and under the oil & gas API6A718 one step aging condition and the traditional two step aging condition. The electrochemical tests were performed in 3.5% NaCl solution and in the NACE TM0177 Solution A (5% NaCl + 0.5% acetic acid). Immersion tests according to ASTM G 48D were used to determine the critical crevice temperature of the alloy. Laboratory results showed that the heat treatment performed to increase the strength of the alloy produced a slight decrease in the resistance to localized corrosion.

1   Introduction

Table 1 shows the composition of some of the nickel alloys used in the Oil & Gas industry mainly because of their high strength and corrosion resistance in sour environments. Except for C-276 (UNS N10276) all the other alloys are precipitation hardenable. The focus of the current work is on the localized corrosion behavior of the nickel alloys used for oil & gas applications, therefore the resistance to environmental cracking or mechanical properties will not be discussed. The pitting resistance equivalent number (PRE) is defined as PRE = %Cr + 3.3(%Mo + 0.5%W) + 16N [1]. In general, the higher the PRE number the higher the resistance of an alloy to localized corrosion such as pitting corrosion or crevice corrosion.

Alloy 945X is generally age hardened to increase its mechanical properties due to the precipitation of gamma prime $Ni_3(TiNbAl)$-type and gamma double prime $Ni_3(NbTiAl)$-type submicron precipitates [2]. Alloy 945X is not considered seawater resistant as per ISO 21457, which requires a minimum PRE of 40 for materials exposed to oxygenated or chlorinated seawater.

Table 1: Nickel Alloys Used in Oil & Gas Applications

Alloy	UNS	Approximate Nominal Composition	PRE
718	N07718	53Ni + 19Fe + 19Cr + 5(Nb+Ta) + 3Mo + 0.9Ti + 0.5Al	29
945X	N09945	53Ni + 15Fe + 21Cr + 3.3Mo + 4Nb + 2Cu + 1.5Ti + 0.2Al	32
625	N06625	58Ni + 5Fe + 20Cr + 8Mo + 3Nb + 1Co + 0.4Ti + 0.4Al	46
C-276	N10276	56Ni + 16Cr + 16Mo + 4W	75
C-22HS	N07022	62Ni + 21Cr + 17Mo	77

Alloy 625 (UNS N06625) is perhaps the most popular nickel alloy in the oil and gas industry. Alloy 625 is extensively used in solid small bore tubing, piping, seals, and valve internals and as overlay cladding on large bore components. Alloy 625 is also age hardenable, that can be used in the annealed (ASTM B444 Grade 1) or solution annealed (ASTM B444 Grade 2) condition, with ultimate tensile strength (UTS) values of 827 and 690 MPa, respectively [ASTM B444]. UNS N06625 is highly resistant to both sweet and sour production fluids and seawater. Reported CPT and CCT values in oxidizing NaCl + HCl environments are 90°C and 50°C, which makes it suitable for the most demanding subsea applications.

Alloy C-22HS belongs to the C family of nickel alloys with an outstanding resistance to localized corrosion [3, 4]. C-22HS is also generally used in the age hardened condition, which increases its mechanical properties through the formation of long-range ordered (LRO) domains of the $Ni_2(Cr,Mo)$ phase [4]. Alloy C-22HS is extremely resistant to all forms of corrosion in aggressive chloride containing environments [5]. Zadorozne *et al.* performed electrochemical testing to measure the general and localized corrosion of C-22HS compared to other Ni-Cr-Mo alloys and they reported that Mo reduced the anodic dissolution rate in the active state and increased the critical potential for the localized corrosion [5]. The crevice corrosion repassivation potential for the tested alloys increased as the PRE increased [5]. Zadorozne *et al.* reported that a heat treatment of C-22HS to increase its mechanical properties only slightly reduced its resistance to crevice corrosion. The crevice repassivation potential in 1 M NaCl at 90°C for mill annealed C-22HS was -134 mV SCE, while for the aged hardened C-22HS it was -177 mV SCE [5]. Similarly, Meck *et al.* reported that the critical crevice temperature (CCT) in 6% ferric chloride ($FeCl_3$) (ASTM G 48 Methods C&D) for mill annealed C-22HS was 100°C and 75°C for the aged hardened condition [6]. In comparison, the CCT for C-276 was 55°C [6].

2 Alloy 718 for Oil & Gas Applications

Alloy 718 (Table 1) has been used initially in aerospace applications, and later has been modified slightly on its composition, thermo mechanical processing and aging heat treatment for oil and gas applications [7]. In upstream oil and gas, alloy 718 uses include rods and tubes for downhole tubing and surface gas-well components, valves, hangers, landing nipples, tool joints and packers [7]. In general oil and gas aimed alloy 718 should have at least 0.8%Ti, 0.4%Al and 4.87% Nb, less than 0.045%C, and ppb levels of P, S, Pb, Se and Bi [8, 9]. Table 2 shows the chemical composition of UNS N07718 according to API 6A718 [8]. Table 3 shows the heat treatment requirements for the two designations 120K and 140K. The minimum hardness for the 120K shall be 32 HRC and 34 HRC for the 140K designation [8]. For

both alloy 718 designations the maximum hardness is limited to 40 HRC to avoid sulphide stress cracking [1, 9].

Table 2: Composition requirements of N07718 per API 6A718

Ni	Cr	Fe	Nb+Ta	Mo	Ti	Al	Maximum
50 to 55	17 to 21	Bal.	4.87 to 5.20	2.80 to 3.3	0.80 to 1.15	0.40 to 0.60	0.045C, 1Co, 0.35Mn, 0.35Si, 0.01P, 0.01S, 0.006B, 0.23Cu, 0.001Pb, 0.0005Se, 0.00005Bi,

Table 3: Heat treatment requirements for N07718 according to API 6A718

Designation	Annealing Temperature	Annealing Time (h)	Age Hardening
120K	1870°F – 1925°F (1021°C – 1052°C)	1 to 2.5 + air cool	1425°F-1475°F (774°C – 802°C) for 6 – 8 hours + air cool
140K	same	same	1400°F-1475°F (760°C – 802°C) for 6 – 8 hours + air cool

2.1 Corrosion Behaviour of Alloy 718

Chen *et al.* studied the effect of thermal heat treatment on the corrosion behavior of alloy 718 [9]. They tested the solution annealed (SA) condition (1026°C or 1879°F for 1.5 h), the BHIA condition (SA + 760°C or 1400°F for 4~5 h plus 650°C or 1202°F for 4~5 h), and the API 6A718 condition (SA + 788°C or 1450°F for 8 h). Chen *et al.* performed electrochemical corrosion tests in nitrogen deaerated 3.5% NaCl at ambient temperature [9]. They reported that the highest corrosion potential was for the SA material (-367 mV SCE) and the lowest corrosion potential was for the APIA material (-419 mV SCE). Similarly, they reported that the highest corrosion rate was for the APIA material (0.03 mm/y) and the lowest for the SA material (0.006 mm/y). In potentiodynamic polarization studies they reported similar passive current and breakdown potential for the three tested materials [9]. However, Chen *et al.* observed a larger amount of pits in the heat treated materials as compared to the SA material, both after the potentiodynamic polarization and after quiescent immersion in naturally aerated 3.5% NaCl solution after one week immersion. For all their studies, the resistance to corrosion ranking was always SA > BHIA > APIA, that is, the one step heat treated material (APIA) seemed to be less corrosion resistance than the two step heat treated material [9].

Wang *et al.* studied the effect of the heat treatment on the cracking susceptibility of alloy 718 at negative applied potentials using the slow strain rate technique at a strain rate of 1×10^{-6} s^{-1} in 0.1M NaCl at 25°C [10]. They tested alloy 718 solution annealed at 1220°C for 1 h and heat treated alloy 718 at 1050°C for 2 h and water quenched. Table 4 shows the results from Wang *et al*. The time to failure and the percentage of intergranular (IG) cracking increased as the applied potential decreased [10]. The heat treated (HT) material was more susceptible to environmentally assisted cracking than the solution annealed (SA) material [10].

Evans *et al.* studied the corrosion behavior of alloy 718 with a hardness of 38.5 HRC and other alloys immersed for 22 weeks in mostly deaerated static and flowing seawater at 30°C [11]. They reported that alloy 718 did not suffer pitting or crevice corrosion and only minor discoloration with general corrosion rates of less than 0.1 mm/y.

However, they cautioned that if crevices are present, alloy 718 may suffer crevice corrosion if the oxygen level rises to the order of 2 to 3 ppm and higher [11].

Table 4: Environmental Cracking of alloy 718 at Cathodic Potentials, Wang et al [10]

Applied potential (mV SCE)	Time to failure (h) 718 SA	Time to failure (h) 718 HT	% IG fracture surface 718 SA	%IG fracture surface 718 HT
Air	252	233	0	0
Open Circuit	251	225	0	0
-900	206	225	4	5
-1050	154	100	20	54
-1200	146	45	23	68
-1350	48	42	81	92

The objective of the current research was to examine the general corrosion and localized corrosion behavior of alloy 718 in the as received (AR) and in two heat treated conditions in deaerated 3.5% NaCl and in NACE TM0177 Solution A.

3   Experimental

The material tested was alloy 718 Heat 2180-1-9954 from a 0.5-inch thick plate (13 mm) (Table 5). The material was tested in the AR condition (hot rolled condition) and in two heat treated conditions. Heat treatment 1 (HT1) was similar to the 120K treatment in Table 3, and heat treatment 2 (HT2) was solution annealing at 980°C for 1 hour followed by water quenching (WQ) plus a two-step aging of 8 h at 720°C followed by 18 hours at 620°C and then air cooled.

Table 5: Tested alloy 718, Heat 2180-1-9954

Ni	Cr	Fe	Nb+Ta	Mo	Ti	Al	Others
53	18.3	18.50	5.21	3.06	1.05	0.50	0.047C, 0.28Co, 0.26Mn, 0.10Si, <0.005P, <0.002S, 0.004B, 0.08Cu, <0.0005Pb, <0.0001Se, <0.00003Bi,

The microhardness of the three materials was measured using a 500 gf load and then converted in the HR scale using ASTM E 140. Table 6 shows the results

Table 6: Micro-hardness of the tested alloy 718, Heat 2180-1-9954

Condition	500 gf micro-hardness	HRC Scale
AR	204, 204, 194	94, 94, 92 HRB
HT1	381, 374, 361	40, 40, 38
HT2	460, 488, 444	46, 48, 46

The electrochemical flat coupons were machined to a dimension of 13 x 13 x 3 mm (0.5 x 0.5 x 0.125 inch). The coupons were ground using SiC paper to a surface finish of 600 grit and then tested in deaerated 3.5% NaCl and NACE TM0177 Solution A (5% NaCl + 0.5% acetic acid). The specimens were mounted in an epoxy resin and then lacquered to expose an area of 1 cm² to the testing electrolyte at ambient temperature. After testing, samples were visually inspected to assure the absence of crevice corrosion under the lacquered areas. Samples displaying crevice corrosion were discarded.

All tests were performed at least three times for each metal condition and electrolyte. The reference electrode was saturated calomel electrode (SCE), and all the potentials are reported in this scale. The equivalent weight of alloy 718 was 26 and the density 8.19 g/cm³. The polarization resistance (PR) tests were conducted according to ASTM G 59 [12] at 0.167 mV/s from -20 to + 20 mV of the instant corrosion potential. The PR tests were used to evaluate the corrosion rate of the materials. The electrochemical impedance (EIS) measurements were conducted according to ASTM G 106 [12] from 10^5 to 0.001 Hz using 10 mV overpotential and generating 10 data points per decade. The cyclic potentiodynamic polarization (CPP) tests were conducted according to ASTM G 61 [12], from -150 mV below the corrosion potential at a scan rate of 0.167 mV/s in the anodic direction. The scan direction was reversed at +1 V SCE or 5 mA/cm² (whichever was reached first). After the tests the samples were studied in a scanning electron microscope. Pitting potentials, E_P, were taken at the inflection point in the forward scan. Repassivation potentials were measured at 1 or 2 $\mu A/cm^2$ and named ER1 and ER2, respectively.

Immersion corrosion tests were used to determine critical crevice temperature following the guidelines in ASTM G 48 method D [12].

4   Results and Discussion

Figure 1 shows the corrosion rate for alloy 718 in the AR, HT1 and HT2 conditions in 5% NaCl + 0.5% acetic acid at ambient temperature. As the immersion time increased the corrosion potential slowly increased. The increase in potential seemed to be faster for the HT2 condition than for the AR condition. As the corrosion potential increased the alloy became more passive and the corrosion rate decreased (Figure 2). That is, the HT2 condition had the lowest corrosion rates. The Bode plot in Figure 3 shows that at the corrosion potential, the three conditions had a similar behavior. At the frequency of 0.001 Hz the impedance of the HT2 material was slightly higher than for HT1 and AR, suggesting a slightly higher corrosion resistance for the HT2 material, which was in agreement with PR results.
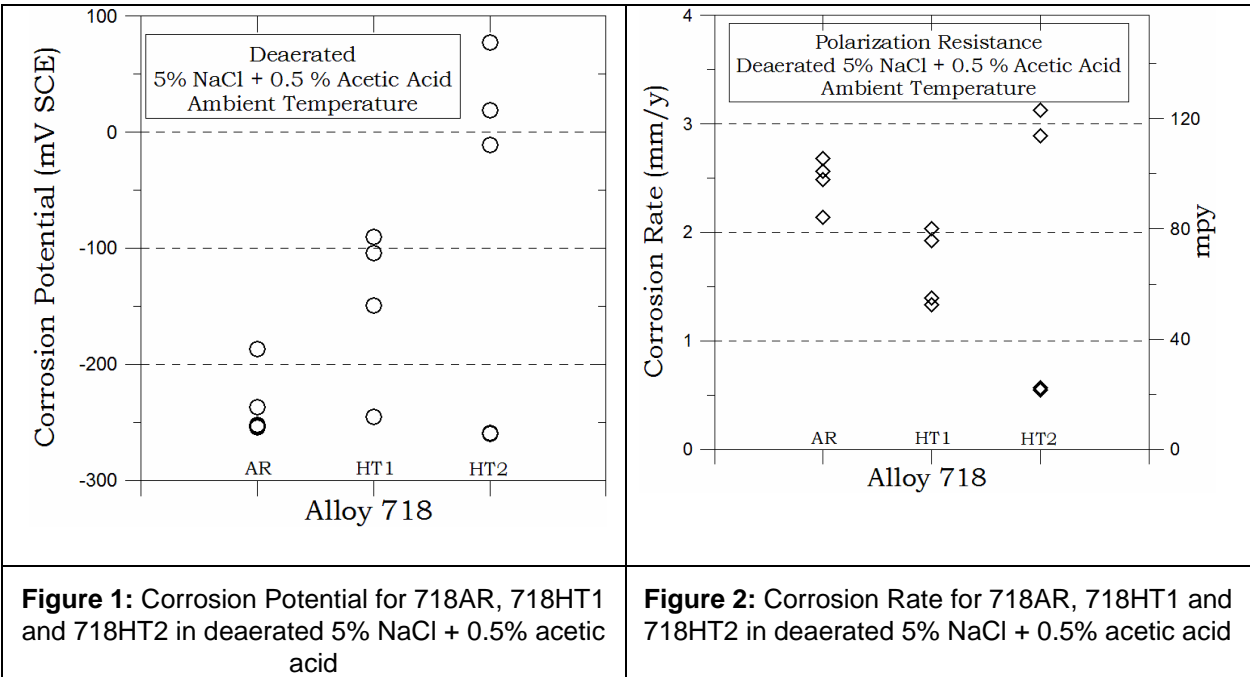

Figure 1: Corrosion Potential for 718AR, 718HT1 and 718HT2 in deaerated 5% NaCl + 0.5% acetic acid

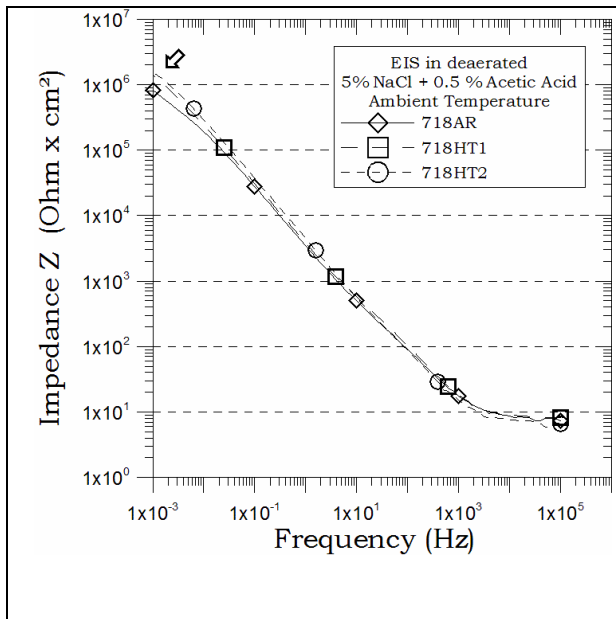**Figure 2:** Corrosion Rate for 718AR, 718HT1 and 718HT2 in deaerated 5% NaCl + 0.5% acetic acid

Figure 3: Bode plot for 718AR, 718HT1 and 718HT2 in deaerated 5% NaCl + 0.5% acetic acid
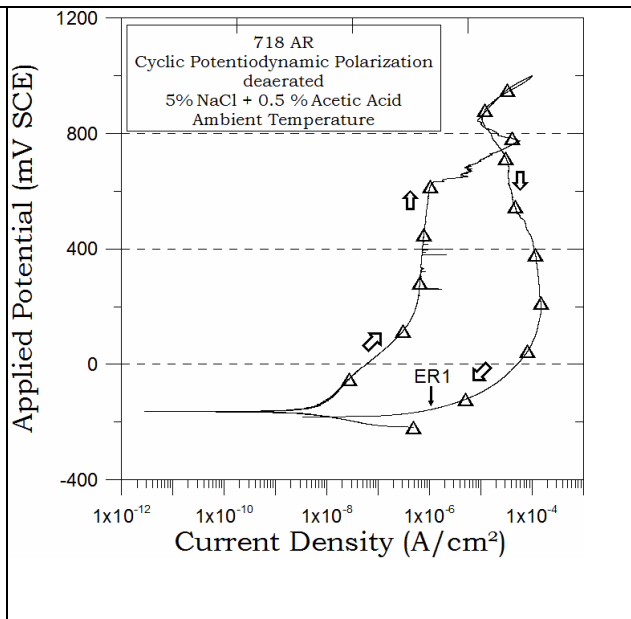
Figure 4: Cyclic Potentiodynamic Polarization (CPP) for 718AR in deaerated 5% NaCl + 0.5% acetic acid

Figure 4 shows the cyclic potentiodynamic polarization (CPP) for 718 AR, with a large hysteresis in the reverse scan, suggesting the presence of localized corrosion such as pitting corrosion. The ER1, which is the potential in the reverse scan for which the current density is 1 µA/cm² may be an indication of the relative resistance to localized corrosion. Qualitatively, the higher ER1 the more resistant the material is to localized corrosion. Figure 4 shows that the value of ER1 was close to the value of the corrosion potential, suggesting that alloy 718 may be susceptible to localized corrosion under open circuit conditions. Figure 5 shows that the values of ER1 for the three materials were similar to each other, suggesting a slight decrease in the resistance to localized corrosion of the heat treated material under the tested conditions.
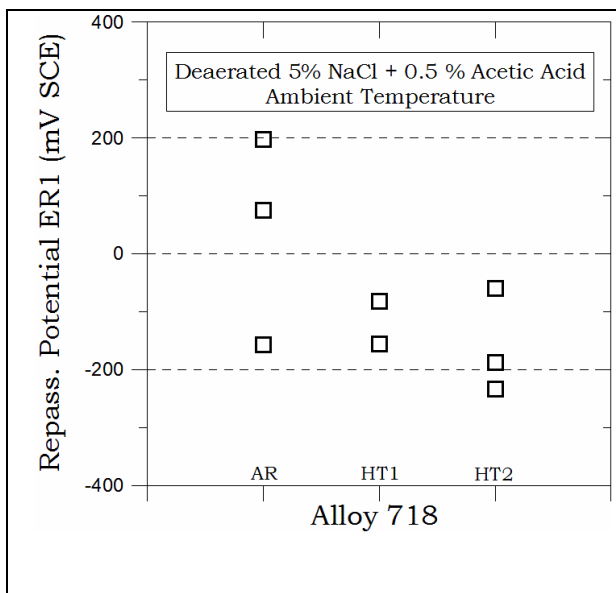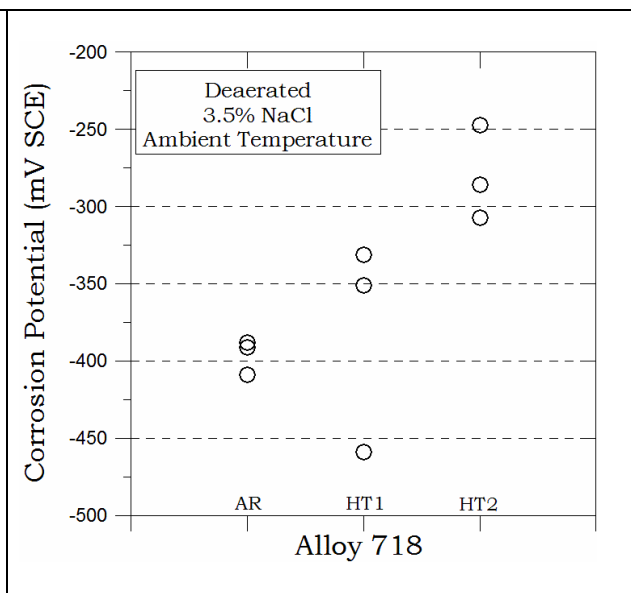

Figure 5: ER1 From the CPP for 718AR,

Figure 6: Corrosion Potential for 718AR,

718HT1 and 718HT2 in deaerated 5% NaCl + 0.5% acetic acid	718HT1 and 718HT2 in deaerated 3.5% NaCl ambient temperature

Figure 6 shows the corrosion potential after one hour immersion for alloy 718 AR, HT1 and HT2 in deaerated 3.5% NaCl at ambient temperature. The corrosion potential was higher for the two heat treated materials, that is, 718 HT2 seemed to passivate faster than the AR received material. This same behavior was observed before for the corrosion potential in the 5% NaCl + 0.5% acetic acid (Figure 1).

Figure 7 shows the CPP for alloy 718 HT2 (repeated three times) in deaerated 3.5% NaCl at ambient temperature. The tests are highly reproducible showing a large hysteresis in the reverse scan suggesting the presence of localized corrosion. The repassivation potential, measured as a cross over potential, ECO, is the potential at which the reverse scan intersects the forward scan. The values of repassivation potential for the three materials in 3.5% NaCl (Figure 8) show a slight decrease for the heat treated materials HT1 and HT2 with respect to the AR material. This behaviour for alloy 718 was reported before in Figure 5 for the TM0177 Solution A (5% NaCl + 0.5% acetic acid). It is likely that the second phase precipitation during the heat treatment act as nucleation for corrosion pits, which later takes longer to repassivate when the potential is decreased. The values of repassivation potential in Figures 5 and 8 may be similar since the concentrations of the two electrolyte solutions are also similar.

Figures 9 and 10 show scanning electron images of the alloy 718 AR and HT1 specimens, respectively, after the CPP tests in 3.5% NaCl at ambient temperature. The HT1 condition had a higher density of pits than the AR condition, even though most of the pits in the HT1 specimen were of smaller size.
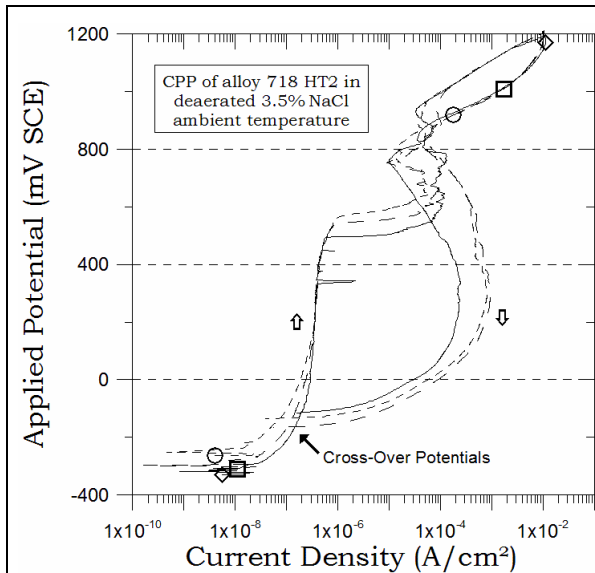

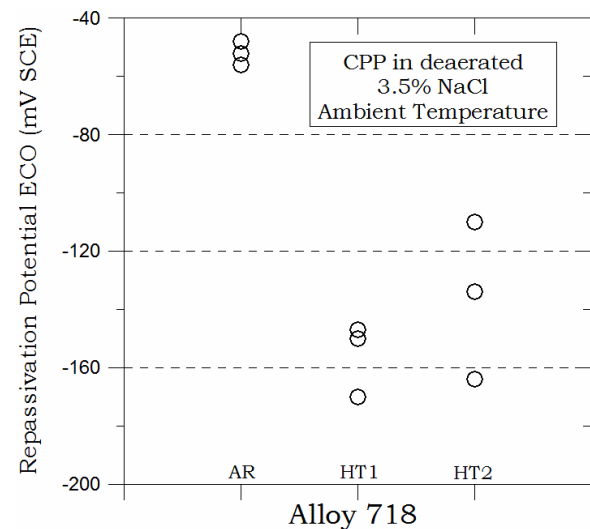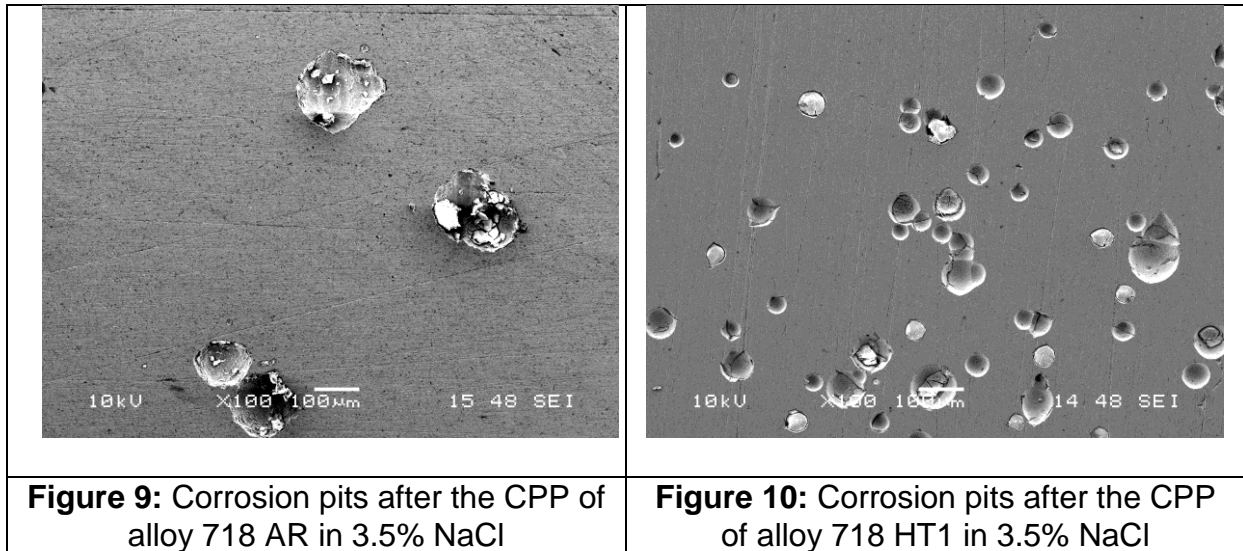| **Figure 7:** CPP in triplicate for 718HT2 in deaerated 3.5% NaCl ambient temperature	**Figure 8:** ECO from the CPP for 718AR, 718HT1 and 718HT2 in deaerated 3.5% NaCl

Figure 9: Corrosion pits after the CPP of alloy 718 AR in 3.5% NaCl	**Figure 10:** Corrosion pits after the CPP of alloy 718 HT1 in 3.5% NaCl

4.1 Localized corrosion behaviour of Alloy 718 vs. C-22HS

The ASTM G 48 standard provides methods for comparing the pitting and crevice corrosion resistance of engineering alloys. The method G 48 D was used to assess the critical crevice temperature (CCT) of both alloys 718 and C-22HS (Table 1) in 6% $FeCl_3$ + 1% HCl, which shall not be confused with the actual maximum service temperatures [12]. The CCT is defined as the temperatures below which crevice corrosion is not expected. The higher the CCT value the higher the resistance of the alloy to crevice corrosion. Both alloys were tested in the mill annealed (MA) condition and the thermally aged condition. The age hardening for C-22HS was performed at 1300°F (704°C) for 16h, furnace cooled to 1125°F (607°C) and treated for 32 h followed by air cooling. The heat treatment for alloy 718 was performed at 1325°F (718°C) for 8h, then furnace cooled to 1150°F (621°C) and kept for 8 h, followed by air cooling. Table 7 shows that the CCT for alloys 718 was much lower than the CCT for C-22HS, as it could be predicted based on their respective PRE values in Table 1. Table 7 also shows that the thermal treatment of both alloys seem to slightly reduce their resistance to crevice corrosion. This observation is in agreement with the electrochemical results shown in Figures 5 and 9.

Table 7: Critical crevice temperatures of 718 and C-22HS – ASTM G 48 D

Alloy	Mill Annealed	Aged Hardened
718	10°C	<10°C
C-22HS	100°C	75°C

5 Summary

Electrochemical tests were conducted using UNS N07718 in the as received condition and in two heat treated conditions both in NACE TM0177 Solution A (5% NaCl + 0.5% acetic acid) and in 3.5% NaCl at ambient temperature. Results from both solutions showed that the three materials have a similar resistance to general corrosion. The heat treated materials, especially HT2 seemed to passivate faster (the E_{corr} raised faster) than the AR material. The heat treatments to increase the strength seemed to slightly decrease the resistance of UNS N07718 to localized corrosion.

This decrease was shown both using cyclic potentiodynamic polarization tests and immersion tests to determine CCT.

6   Acknowledgements

7   References

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