Crevice corrosion of nickel superalloy in deaerated chloride/sulphate solution at 90°C

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Abstract. Alloy 22 is a nickel base alloy highly resistant to all forms of corrosion. It was designed to resist to most aggressive environments for industrial applications. Electrochemical studies such as Potentiodynamic-Galvanostatic-Potentiostatic (PD-GS-PD) tests and Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM) observations were performed to determine the corrosion behaviour of alloy 22 (N06022). The effect of sulphate ion in chloride containing solutions at 90°C, were studied in this work under aggressive conditions where this material might be susceptible to crevice corrosion. The electrolyte solution, which consisted of 0.1M and 1M NaCl and different sulphate concentrations. It was observed that there were complete inhibitions of crevice corrosion for RCRIT=[SO₄²⁻]/[Cl⁻]=1 in the 0.1mol/L NaCl solutions and RCRIT=2 in the 1mol/L NaCl solutions. The corrosion rate obtained was about 0.1μm/year at 24 hours of immersion.

1. Introduction
Alloy 22 (UNS N06022) belongs to the Ni-Cr-Mo family, and it is extremely resist to general and localized corrosion [1-2]. It contains nominally 22% Chromium, 13% Molybdenum and 3% Tungsten. Alloy 22 is generally not susceptible to pitting corrosion in chloride solutions, however, it might suffer crevice corrosion under certain aggressive conditions [3-5]. The localized corrosion will only occur when the corrosion potential is equal or higher than a critical potential. The susceptibility to crevice corrosion is measured by the value of repassivation potential E₉,CREV, in each tested condition. The crevice corrosion repassivation (E₉,CREV) potential has been proposed as the critical potential [6]. Chloride is the only known ion that is able to promote the crevice corrosion of Alloy 22 [5,7-8]. The alloy susceptibility to crevice corrosion is increased by temperature and higher chloride concentrations. Species such as nitrate, carbonate, hydroxyl, phosphate, Fluoride, organic acids are also able to mitigate or inhibit the crevice corrosion [2,5-6,9-10]. In the literature, there is a critical concentration ratio RCRIT = [Inhibitor]/[Cl⁻] for the inhibition to be complete. The lower the RCRIT value, the better the effectiveness of the inhibitor. RCRIT for nitrate is 0.15 to 0.5 while RCRIT for fluoride is 5 to 10, and it is 5 to 20 for organic acids [11-12]. The occurrence of crevice corrosion is due to the formation of a hydrochloric acid solution in the creviced region. Inhibitors act by eliminating the occurrence of hydrochloric acid or by hampering its actions [13]. Different standardized techniques have a been used for determining E₉,CREV for alloy 22, such as cyclic potentiodynamic polarization (CPP) [14] technique (ASTM G6), Tsujikawa – Himasatsu Electrochemical (THE) method (ASTM G192) [14]. Non-standardized techniques, such as Potentiodynamic-Galvanostatic-Potentiodynamic PD-GS-PD [15], have been also used. The objective of this work was to evaluate the general and
crevice corrosion performance of Alloy 22 in solutions containing different concentration of chloride and sulphates at 90°C, by PD-GS-PD technique. The repassivation potentials were used as the parameter for comparison of the crevice corrosion susceptibility.

2. Experimental procedure

The chemical composition of the Alloy in Weight percent was 59.56% Ni, 20.38% Cr, 13.82% Mo, 2.64% W, 2.85% Fe, 0.17% V, 0.16% Mn, 0.008% P, 0.0002% S, 0.05% Si, and 0.005% C. Electrochemical measurements were carried out using a glass cell. A platinum foil was used as a counter-electrode. A saturated calomel electrode was used as a reference (SCE) (\(V_{sce}=V_{NHE}+0.244V\)). Two different types of specimens, prismatic and PCA (Prism Crevice Assembly), were used to study uniform and crevice corrosion behaviour respectively. I) Prismatic specimen for the study of corrosion in the passive state. II) PCA (Prism Crevice Assembly) specimen with crevice formers of PTFE-coated ceramic material (ASTM G 78) [14], especially designed for the study of crevice corrosion. The samples were polished with SiC sandpaper to particle size 600, rinsed with alcohol and water and then dried with a stream of air. The studied solutions included chloride 0.1M, 1M plus different concentrations of Na\(_2\)SO\(_4\). The tests temperature was 90°C. Oxygen was eliminated by N\(_2\) bubbling. Potentiodynamic-Galvanostatic-Potentiodynamic (PD-GS-PD) tests were performed using PCA specimen to establish crevice corrosion susceptibility. PD-GS-PD test consisted of three consecutive stages [15]: (1) A potentiodynamic polarization (at 0.167mV/s) in the anodic direction up to reaching an anodic current of 30\(\mu\)A. (2) Application of a constant anodic current of \(I_{gs}=30\mu\)A for 2h. (3) A potentiodynamic polarization (at 0.167mV/s) in the cathodic direction, from the previous potential up to reaching alloy repassivation. General or uniform corrosion rates were obtained by means of Electrochemical Impedance Spectroscopy (EIS). The scan started from 10kHz to 1mHz. EIS measurements were performed after 1 hour and 24 hours of immersion. Simple equivalent circuits were fitted to the experimental data in order to obtain the polarization resistance \((R_p)\) and calculate the corrosion rate \((CR)\), using Equation 1.

\[
CR(\mu m/\text{year}) = \frac{K \cdot EW \cdot B}{\rho R_p}
\]

Where K is the faradic conversion constant \((K=3.27*10^6\mu \text{mgA}^{-1}\text{cm}^{-1}\text{year}^{-1})\), B is the Stern and Geary constant, EW is the Equivalent Weight \((EW=23.28)\), \(\rho\) is the alloy density \((\rho=8.69g/cm^3)\) and \(R_p\) is the polarization resistance. At the end of the tests, the specimens were examined in the optical and scanning electron microscopes (SEM).

3. Results and discussion

Figure 1 shows PD-GS-PD tests on Alloy 22 in 0.1mol/l NaCl+Na\(_2\)SO\(_4\) solutions at different R values. The three stages as described above are observed. The PD-GS-PD technique provides a cross-over potential \((E_{R,CREV})\) which is determined at the intersection of the forward (stage 1) and reverse (stage 3) scan. When the no cross-over between the forward and the reverse scans, \(E_{R,CREV}\) was determined at the intersection of the reverse scan and the extrapolation of the passive current in the forward scan at higher potentials. Eco increased as R increased. The potential drop during the galvanostatic step was negligible for R=1 suggesting crevice corrosion did not occur, which was verified by SEM. Figure 2 Shows \(E_{R,CREV}\) of Alloy 22 as a function of R, for chloride plus sulphate solutions. The values of \(R_{CRIT}\) were dependent of the chloride concentration in this case. \(R_{CRIT}=1\) and \(R_{CRIT}=2\) were found for 0.1M and 1M chloride solutions, respectively. Sulphate has been studied as an inhibitor of localized corrosion (pitting) of stainless steels. Sulphate cannot be reduced within an acidic solution and it is stable as SO\(_4^{2-}\) or HSO\(_4^-\). The sulphate ions can act mainly as supporting electrolytes, slowing the accumulation of chloride. The above, involves the competitive migration and adsorption of sulphate and chloride on the alloy surface [16]. Sulphate accumulates at the alloys/solution interface by
migration due to its higher charge in relation to ions chloride concentration, which prevents the increase of chloride concentration above a $R_{CRIT}$ [13].

**Figure 1.** PD-GS-PD tests for Alloy 22 in 0.1M NaCl solutions with different Na$_2$SO$_4$ additions at 90°C.

**Figure 2.** $E_{R,CREV}$ as a function of $R$ for Alloy 22 in chloride plus sulphate solutions (pH 5.5 to 6.5) at 90°C.

Crevice corrosion was found in all solutions with ratios lower to $R_{CRIT}$. The attack was always located below the crevice formers (see Figure 3(a)). This type of attack is named crystalline, since the different crystal planes corrode at different rates. Alloy grains can be seen in some areas (see Figure 4). For PD-GS-PD method the Extent of the localized corrosion (crevice) attack was limited by the current set in stage 2. Corrosion products appeared around to areas affected by localized corrosion. There was no crevice corrosion for $R \geq R_{CRIT}$ (see Figure 3(b)).

**Figure 3.** Photographs and SEM images of Alloy 22 after PD-GS-PD curves in different solutions: (a) 0.1M NaCl+0.05M Na$_2$SO$_4$ (b) 0.1M NaCl+0.1M Na$_2$SO$_4$.

**Figure 4.** SEM Images of Alloy PCA specimens after a PD-GS-PD curves in 0.1M NaCl+0.05M Na$_2$SO$_4$ solution.

Instantaneous corrosion rates were calculated using the parameter $R_P$, which was obtained by fitting simple equivalent circuits to the EIS data. Tests were performed after 1 hour and 24 hours immersion in naturally aerated solutions. There was a lower corrosion rate (0.1µm/year) for the 24-hour period when compared to the 1-hour period in all the analysed environments (see Figure 5).
4. Conclusions

Crevice corrosion inhibition was observed in the Alloy 22 in solutions containing chloride and sulphates from a concentration ratios $R=1$ and $R=2$ for 0.1M and 1M chloride solutions, respectively.

With the use of PD-GS-PD technique, $R_{CRIT}$ conservatives were obtained in comparison with other electrochemical techniques.

Low corrosion rates at 24 hours were determined, independent of the sulphate concentration.

References

[1] R B Rebak 2000 Corrosion and environmental degradation vol 2, ed M Schutze (Weinheim: Wiley-VCH) pp 69-111
[2] R M Carranza 2008 JOM 60 58
[3] G M Gordon 2002 Corrosion 58(10) 811
[4] R M Carranza 2008 Proceeding Corrosion/2008 (Houston: NACE Intl) 08580
[5] D S Dunn, Y M Pan, K T Chiang, L Yang, G A cragnolino, X He 2005 JOM 57 49-55
[6] R B Rebak 2005 Proceeding Corrosion/2005 (Houston: NACE International) 05610
[7] B A Kehler, G O Ilevare, J C Scully 2001 Corrosion 57 1042-1065
[8] G.O Ilevare 2006 Corrosion 62 340-356
[9] M Miyagusuku, R M Carranza, R B Rebak 2015 Corrosion 71 574-584
[10] D S Dunn, L Yang, C Wu, and G A Cragnolino 2004 Scientific Basis For Nuclear Waste Management XXVIII vol 824 ed J M Hanchar, S Stroes–Gascoyne and L Browning (Warrendale: Mater. Res. Soc. Proc.) pp 33-38.
[11] R B Rebak 2009 Corrosion 65(4) 252-271
[12] G O Ilevare, K J King, S R Gordon, H A Elayat, G E Gdowsky, T S E Gdowsky 2005 J Electrochem. Soc. 152(12) B547
[13] J R Galvle 1976 J Electrochem Soc. 123(4) 464-474
[14] V A Mayer 2010 Annual Book of ASTM standard section 3 vol 2, ed S J Bailey, N C Emery, J Ermigietti, D Gallagher, K Hanratty, E Moore, E A Olcese, K A Peters, J L Rosiak, D A Terruso, J Wright (West Conshohocken: ASTM International) pp 315-323
[15] A K Mishra, G S Frankel 2008 Corrosion 64(11) 83
[16] C S Brossia, R G Kelly 1998 Corrosion 54 145