

Environmentally Assisted Cracking of Nickel-Based UNS N09955 in Saltwater with Cathodic Protection for High-Pressure, High-Temperature Applications

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**ABSTRACT**

A thorough characterization of nickel-based UNS N09955 was performed in saltwater with cathodic protection (SWCP) environment for high-pressure high-temperature (HPHT) subsea applications. The test environment was deionized water with 3.5% NaCl, pH of 8.2, CP potential of  $-1,050$  mV vs. saturated calomel electrode, and at  $40^{\circ}\text{F}$  ( $4.4^{\circ}\text{C}$ ).

Environmentally assisted cracking susceptibility of the alloy was evaluated by performing fracture toughness test using compact tension test specimen and rising displacement method in air and in SWCP as well as fatigue crack growth rate (FCGR) and static crack growth rate (SCGR) in SWCP. Fracture toughness test in SWCP conditions indicated a significant reduction in the initiation fracture toughness value of the alloy in SWCP versus in-air values. FCGR by performing frequency scan at various  $\Delta K$  values and SCGR of the alloy was studied in SWCP condition. SCGR was obtained at different load holds of 55, 66, 75, and 99  $\text{MPa}\sqrt{\text{m}}$  and various CP potentials of  $-1,050$ ,  $-1,000$ ,  $-950$ , and  $-900$  mV. No crack growth was observed at 55  $\text{MPa}\sqrt{\text{m}}$ , and a crack growth rate (CGR) of  $2 \times 10^{-7}$  mm/s was established at  $-1,050$  mV CP potential. By changing the load and electrode potential, CGR was varied. The obtained results were also compared with other precipitation hardened nickel alloy behavior.

Finally, scanning and transmission electron microscopy (SEM and TEM) were used to characterize the fracture surface morphology, grain structure, and grain boundary precipitates, as well as the shape, size, and distribution of the precipitates.

Key words: cathodic protection, fracture toughness, fatigue crack growth rate, static crack growth rate, hydrogen embrittlement, hydrogen stress cracking, precipitation hardened, nickel-based alloys

## INTRODUCTION

Precipitation hardened (PH) Ni-based alloys have been utilized in oil and gas industry for decades. Among them, UNS<sup>1</sup> N07718 because of its performance in sour wellbore fluids and in hydrogen charging environments has received the most attention for multiple upstream applications such as tubing hangers, production stab, multi-phase flow meter bodies, valve stems, etc. It has been reported that the alloy performance is generally acceptable for many applications up to 175 °C (350 °F) – 204 °C (400 °F) in the exposed wellbore environments such as sour production fluid, completion brine, and depending on metallurgical processing and microstructure externally exposed to SWCP at the seabed temperature. However, at higher temperatures, it becomes vulnerable to localized corrosion and stress corrosion cracking (SCC) especially in low pH and higher chloride containing production environments.<sup>1</sup> Studies have shown that other well-known corrosion resistant alloys (CRA's) such as UNS N07725 (Alloy 725) or UNS N07716 (Alloy 625+) are more susceptible (in comparison to UNS N07718) to hydrogen stress cracking (HSC) in SWCP condition due to formation of the grain boundary precipitates such as sigma phase and carbides.<sup>2-5</sup> Therefore, these alloys which have excellent resistance to localized corrosion and stress corrosion cracking in elevated sour production fluids, are not suitable for the applications that the material is exposed to SWCP externally. With the development of high-pressure, high-temperature (HPHT) fields, experiencing the exposure to high temperature wellbore fluid internally and SWCP externally become inevitable, and the industry needs to look for proper alloy or alloys that withstand these complicated situations.

Ni-based CRA's generally exhibit excellent resistance to uniform corrosion over a wide range of pH's, chloride concentrations, and temperatures. They can however be susceptible to localized corrosion, and SCC at elevated temperatures in the presence of aggressive environments containing chlorides/ and acid gases such as H<sub>2</sub>S and CO<sub>2</sub>. The susceptibility of these alloys to localized corrosion and SCC is related to the repassivation potential behavior. When the potential (applied or corrosion potential) is below the repassivation potential, alloys are generally found to be resistant to localized corrosion and SCC. However, when the potentials are above the repassivation potential, the alloys are susceptible to localized corrosion and SCC. In several cases localized corrosion sites such as pits, were found to be sites where SCC would initiate. SCC susceptibility is typically determined based on either slow strain rate (SSR) or constant deflection tests like C-ring test. Under the same conditions, SSR tests are more aggressive than the constant deflection tests. In addition, the susceptibility to SCC was found to be dependent on the applied strain rate in the SSR tests. These observations clearly suggest that the applied strain rate plays a critical role establishing the susceptibility of CRA's to SCC. In HPHT conditions, materials are subject to not only aggressive environments, but a complex set of loading conditions that involves high static loads coupled with low cycle fatigue events. Hence, to accurately reflect the material response in service conditions, it is important to determine the fracture toughness and FCGR and characterize the materials behavior under various loading regimes.

UNS N09955 was introduced recently and showed low corrosion rate and less susceptibility to localized corrosion and SCC in NACE<sup>2</sup> MR0175-3 VII sour environment with addition of free elemental sulfur (S<sup>0</sup>) when tested per NACE TM0177 standard, and borderline elongation to failure ratio results in a hydrogen charging condition when tested per NACE TM0198.<sup>6,7</sup> UNS N09955 microstructure and mechanical properties were characterized after different heat treatments. TEM study of the microstructure using image analysis technique exhibited that there were only  $\gamma''$  particles when heat treated at 746 °C (1375 °F). However, with the additional heat treatment at 621 °C (1150 °F) a higher total volume fraction of  $\gamma'' + \gamma'$  appeared in the microstructure and yield strength of the material increased 15 percent.<sup>8</sup>

Since UNS N09955 developed recently, lacks information about its environmental behavior under varying loading condition. Limited previous studies suggest that it might be a candidate replacing other alloys that are vulnerable in an aggressive HPHT environment. Therefore, the goal of this research is to characterize the alloy's behavior in saltwater under cathodic polarization by performing fracture toughness, fatigue and static crack growth rate tests and studying its microstructure using advanced analytical tools.

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(1) Unified Numbering System (UNS) for Metals and Alloys. Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International).

(2) NACE (AMPP), 15835 Park Ten Pl, Houston, Texas 77084

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## EXPERIMENTAL PROCEDURE

The test program consisted of characterizing UNS N09955 in SWCP condition by performing the following experiments and analysis.

- Fracture toughness (FT) tests in air and in SWCP at 4.4 °C (40 °F) using rising displacement method
- Fatigue crack growth rate (FCGR) test in SWCP environment
- Static crack growth rate (SCGR) test in SWCP environment
- Advanced microstructural characterization using SEM and TEM

### Test Material

Experiments and studies were performed on a forged bar of alloy 955-120K with 483 mm (19 in) diameter. Chemical composition (from the product analysis) and mechanical properties of the material are given in Tables 1 and 2 respectively.

**Table 1: Chemical composition of the alloy 955**

| Element   | C         | Mn       | Si       | Cr        | Ni        | Mo      | S          | P         | Cu        | Co       | Al        | Ti        | Nb      | B          | Fe   |
|-----------|-----------|----------|----------|-----------|-----------|---------|------------|-----------|-----------|----------|-----------|-----------|---------|------------|------|
| API 6ACRA | 0.030 max | 0.50 Max | 0.50 max | 20.0-24.0 | 55.0-60.0 | 5.5-7.0 | 0.0010 max | 0.015 max | 0.044 max | 1.00 max | 0.25-0.80 | 0.50-1.00 | 4.0-5.5 | 0.0060 max | Bal. |
| The Alloy | 0.008     | 0.08     | 0.10     | 21.7      | 57.3      | 5.9     | <0.0004    | 0.004     | 0.043     | 0.01     | 0.45      | 0.80      | 4.8     | 0.0029     | 8.8  |

**Table 2: Mechanical properties of the material**

| Tensile properties at M.R. and longitudinal direction at 68 F |           | Hardness  |      | Grain Size |         | M.R. and transverse (C-L) direction at -76 F |  | Lateral Expansion   |  | Shear         |  |
|---------------------------------------------------------------|-----------|-----------|------|------------|---------|----------------------------------------------|--|---------------------|--|---------------|--|
| Y.S. at 0.2% (ksi)                                            | UTS (ksi) | %El. (4D) | % RA | HRC        | average | CVN Impact values (ft.lb)                    |  | Inches              |  | %             |  |
| 130                                                           | 162       | 39        | 54   | 36-38      | 2 – 3   | 75, 77, 76                                   |  | 0.031, 0.033, 0.033 |  | 100, 100, 100 |  |

### Test Specimens

Compact tension test (CT) specimens were extracted from mid-radius (or T/4, where T is the thickness) location and in L-R orientation with the notch direction running from outer surface to inner surface (OD to ID). CT specimens used for FT and CGR tests are illustrated in Figures 1 and 2.

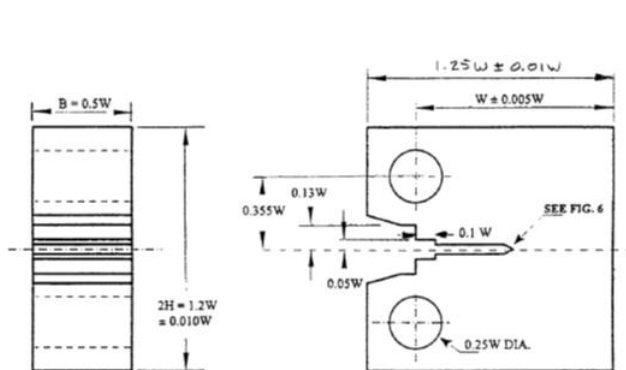


**Figure 1: FT test specimen geometry in accordance with ASTM<sup>(3)</sup> E1820.<sup>9</sup>**

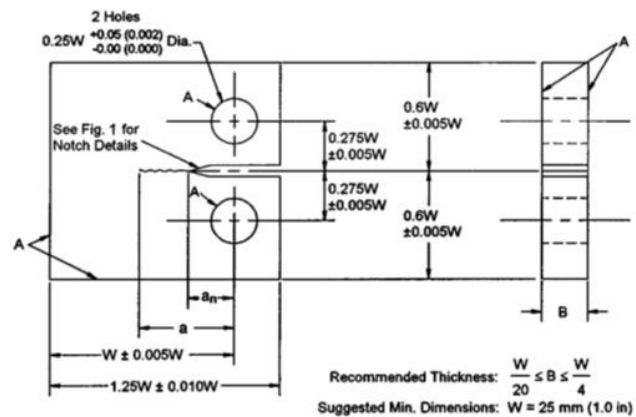


**Figure 2: FCGR and SCGR test specimen in accordance with ASTM E647.<sup>10</sup>**

The dimension and properties the specimens used for FT testing to determine J-R curve (hereafter, JCT) and the specimens used for crack growth rate studies are given in Table 3.

<sup>(3)</sup> ASTM, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA 19428-2959, USA

**Table 3: Dimension and pre-cracking condition of the FT and CGR test specimens**

| Specimen | W (mm) | B (mm) | a <sub>notch</sub> (mm) | a/W <sub>final</sub> | Side Groove (%) | Pre-cracking parameters |                          |     |        |
|----------|--------|--------|-------------------------|----------------------|-----------------|-------------------------|--------------------------|-----|--------|
|          |        |        |                         |                      |                 | $\Delta a$ (mm)         | K <sub>max</sub> (MPavm) | R   | f (Hz) |
| JCT      | 25.4   | 12.7   | 12.7                    | 0.55                 | 5               |                         |                          |     |        |
| CT       | 50.8   | 25.4   | 16.51                   | 0.35                 | 5               | 1.27                    | 27.5                     | 0.2 | 0.3    |

Pre-cracking was performed using servo-hydraulic test machine with the parameters given in Table 3. After pre-cracking, the specimens were side grooved to avoid crack branching and out of plain crack growth.

### Test Environment

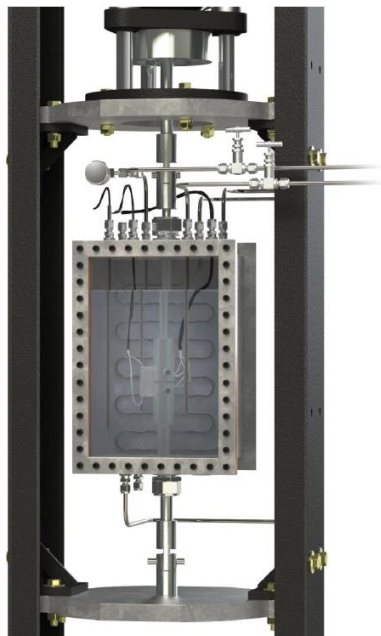
The tests to determine hydrogen embrittlement susceptibility of the material were conducted in deaerated and deionized SWCP environment given in Table 4.

**Table 4: The test environment condition**

| Parameter | NaCl (wt.pct.) | Reference Electrode | Electrode Potential (mV) | pH       | T, °C (°F) | Dissolved Oxygen |
|-----------|----------------|---------------------|--------------------------|----------|------------|------------------|
| Value     | 3.5            | SCE                 | -1050                    | 8.2 ±0.2 | 4.4 (40)   | Deaerated        |

### Test Vessel

Experiments were performed in a 12-L rectangular cell made of UNS N10276 that mounted in a load frame. A recirculating fluid with a mixture of water and glycol was used to maintain the required test temperature of 4.4±1°C (40 °F± 1.8 °F). To maintain a uniform temperature in the cell, the coils carrying the mixture were uniformly spaced through the height of the cell. To avoid galvanic coupling, the CT specimens were loaded to the load train with electrically isolated using ceramic coating pins and alloy UNS N10276 clevises. Figure 3 shows an illustration of the test vessel and the test setup.

**Figure 3: Schematic illustration of FT and FCGR test vessel and the tests set up.**

### Fracture Toughness Tests

Three fracture toughness (FT) tests were performed using rising displacement method per ASTM E1820<sup>9</sup> standard. One FT test was performed in air and two FT tests were performed in SWCP environment to determine the property deterioration with respect to in-air values. The crack length was measured using direct current potential drop

(DCPD) method. Loading rate, K-rate, for in-air FT test was about  $5 \text{ N.mm}^{-3/2}/\text{s}$  and for in-SWCP environment tests was  $0.005 \text{ N.mm}^{-3/2}/\text{s}$  to allow sufficient time for the reactions and processes in the environment to interact with the fracture process zone enabling a proper study of hydrogen embrittlement (HE) and environmentally assisted cracking (EAC) susceptibility of the material. Load, crack mouth opening displacement (CMOD) and crack length were measured during the experiments. CMOD for the tests was determined by correcting the load line displacement for any extraneous displacement from the frame stiffness for the given sample geometry and temperature. Then J- $\Delta a$  curve was determined for each test and fracture toughness was calculated in term of stress intensity factor for sum of the elastic and plastic components in accordance with the equations given in the standard. Poisson ratio and modulus of elasticity were considered 0.31 and 204,000 MPa (29,588 ksi) respectively. J and K<sub>I</sub> values were determined at crack extensions of 0 mm (threshold), 0.2 mm, 0.5 mm, 1 mm, and maximum load.

### Crack Growth Rate Test

A single specimen was used to characterize alloy 955 environmentally assisted FCGR and SCGR properties. The test was performed under stress intensity factor, K, control and the targeted K/dK values were controlled and adjusted throughout the test as the crack propagated. Loading was started at K<sub>max</sub> of 55MPa√m, and an R-ratio of 0.5 under cyclic loading using an asymmetrical (saw tooth) wave form with a 9:1 rise to fall time as shown in Figure 4 schematically. The experiment was commenced at 0.1 Hz frequency, corresponding to a 9-second rise and 1-second fall time. Once sufficient crack growth (50-100 μm depending on the crack growth rate) was established the test was transitioned to 0.01 Hz corresponding to 90 second rise and 10 second fall time and then to 1 mHz (900 s rise and 100 s fall time). Subsequently, 9000 seconds and 86400 seconds hold times were introduced under 1 mHz cycling (900 s rise and 100 s fall time) to understand the effect of hold times. The test was finally transitioned to constant K conditions. Subsequently the K<sub>max</sub> was increased to 66MPa√m, at a R-ratio of 0.5 under cyclic loading conditions similar to 55MPa√m. The test was transitioned through hold periods to constant K conditions and the effect of applied potential was explored from -1050mV SCE to -900mV SCE. Following this, a similar sequence was adopted to characterize the fatigue and static crack growth behavior at 75 MPa√m, and 99 MPa√m, as well as understand the effect of applied potential on the static crack growth behavior.

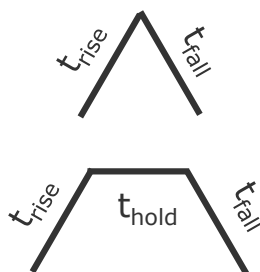


**Figure 4: Schematic illustration of loading waveform (triangular wave form) with the loading rise, fall, and hold times applied in the frequency scan tests.**

### Specimen Preparation for SEM Examination – Microstructure Characterization

A sample from the FCGR/SCGR specimen tested in SWCP condition was sectioned using electrodischarge machining (EDM) into two parts as shown in Figure 5. A portion of Section A was further cut using EDM, mounted and polished to perform microstructural characterization of crack propagation path as shown in Figure 6. This section was prepared using mechanical grinding and polishing. The final polishing step included polishing using colloidal silica suspension to obtain deformation free surface. Section B was cracked open in a load frame to perform fracture surface analysis.

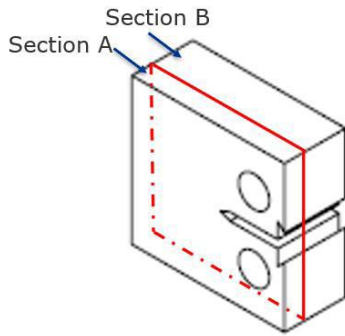


**Figure 5: Sectioned CT specimen for advanced SEM studies. Section A dimensions - B/3, Section B dimensions – 2B/3 (B is the specimen thickness).**

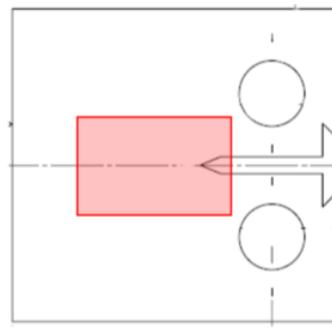


**Figure 6: Cross section examination of crack propagation path studies using SEM.**

## RESULTS and DISCUSSION

### Fracture Toughness Tests

Results of the slow rising displacement tests (one in air and two in SWCP) are shown in Figures 7 and 8. The experiments in SWCP environment were performed at K-rate of  $0.005 \text{ N.mm}^{-3/2}/\text{s}$  in accordance with API 17TR8<sup>11</sup> recommendations. Load-CMOD and corresponding J-R curve shows a smooth behavior with no evidence of pop-ins.

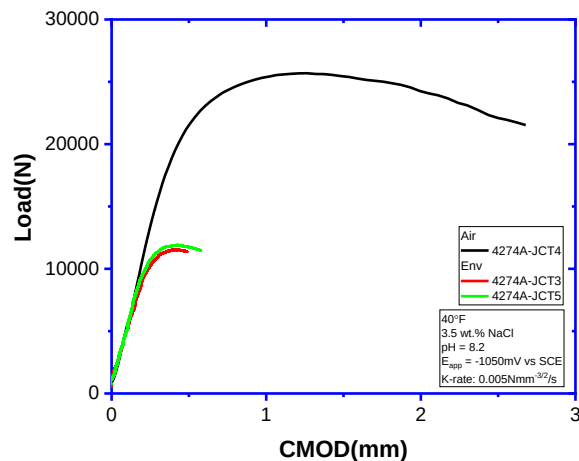


**Figure 7: Load-CMOD curves of the alloy 955 in-air and in SWCP condition.**

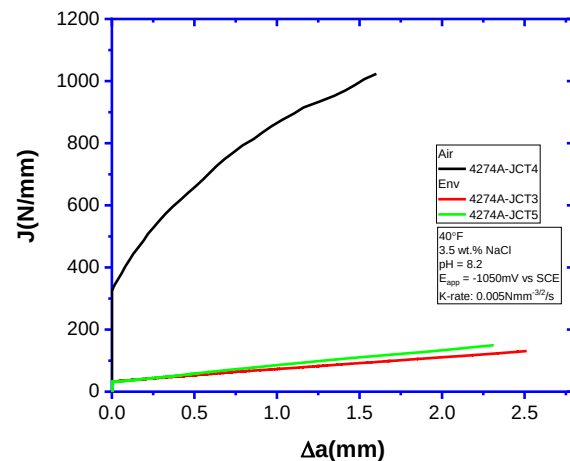


**Figure 8: Corresponding J-R curves of the alloy 955 in-air and in SWCP condition.**

The slope of the J-R curves in SWCP condition is significantly shallower than the slope of J-R curve in air. The initiation fracture toughness parameter,  $J_{th}$ , as and  $J_{0.2 \text{ mm}}$  (J at 0.2 mm crack extension) were found to be 31 N/mm and 41.5 N/mm respectively which indicate a significant drop with respect to in-air values.  $J_{th}$  and  $J_{0.2 \text{ mm}}$  and corresponding  $K_J$  values for the specimens tested in air and in SWCP are given in Table 5.

**Table 5: summary of fracture toughness values obtained for the material in air and in SWCP using rising displacement method**

| Specimen ID | Environment | K-rate<br>( $\text{N.mm}^{-3/2}/\text{s}$ ) | $J_{th}$<br>(N/mm) | $K_{Jth}$<br>( $\text{MPa}\sqrt{\text{m}}$ ) | $J_{0.2 \text{ mm}}$<br>(N/mm) | $K_{J0.2 \text{ mm}}$<br>( $\text{MPa}\sqrt{\text{m}}$ ) | $J_{maxload}$<br>(N/mm) | $K_{Jmaxload}$ |
|-------------|-------------|---------------------------------------------|--------------------|----------------------------------------------|--------------------------------|----------------------------------------------------------|-------------------------|----------------|
| 4274A-JCT4  | Air         | 5                                           | 343.39             | 279.01                                       | 381.92                         | 339.33                                                   | 529.4                   | 346.43         |
| 4274A-JCT3  | SWCP        | 0.005                                       | 32.56              | 85.92                                        | 40.85                          | 96.24                                                    | 102.8                   | 152.66         |
| 4274A-JCT5  | SWCP        | 0.005                                       | 30.87              | 83.66                                        | 41.26                          | 96.72                                                    | 106.2                   | 155.16         |

The measured J-R curves were converted to  $K_J$  vs CGR (da/dt) measurements and the results are shown in Figure 9. The crack growth rate was estimated by finding the slope of the crack length vs time plot for small increments of crack extension ( $50\mu\text{m}$ ). The average  $K_J$  value in this time period was assigned to the estimated crack growth rate. The results indicate that the  $K_{Jth}$  is about  $86\text{MPa}\sqrt{\text{m}}$  and the crack growth rate exhibits a  $K^2$  dependence. The crack growth rate of nickel based alloys under cathodic polarization is known to be a function of the applied K-rate.<sup>12</sup>

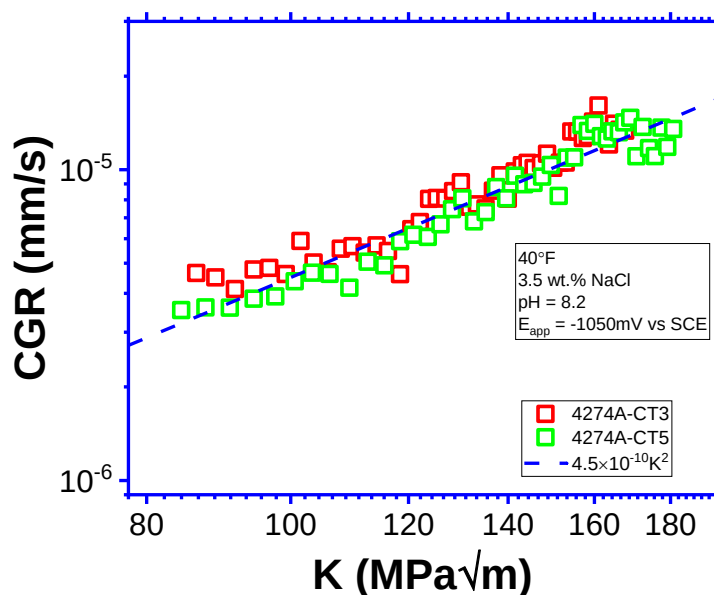


Figure 9: CGR versus K plot obtained from rising displacement J-R curves.

### Post-Test Fractography

Fracture surface of the specimens was studied using SEM. In-air tested sample (4274-JCT4) exhibited ductile fracture morphology of cup and cone associated with dimples, shown in Figure 10.

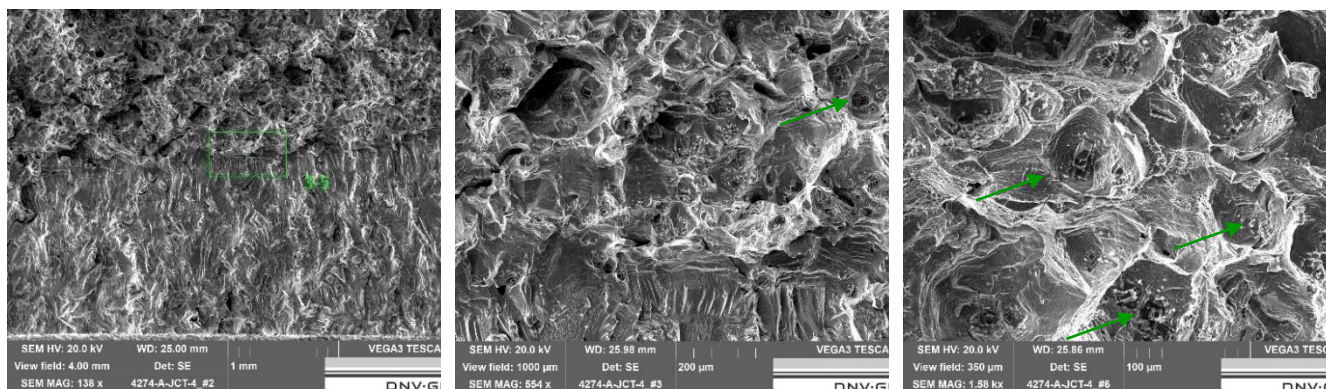


Figure 10: Post-test fracture surface study of 4274-JCT4 specimen which was tested in-air. The specimen exhibits cup and cone ductile fracture features (dimples) shown with green arrows.

The specimens tested in SWCP environment indicated intergranular cracking with evidence of dislocation slip band (DSB) cracking as shown in Figure 11 (4274-JCT3) and Figure 12 (4274-JCT5).