

Comparison of Hydrogen Embrittlement Testing Methods of UNS N07718

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ABSTRACT

The hydrogen embrittlement susceptibility of several UNS N07718 microstructures was determined with different *in situ* testing techniques. Hydrogen-affected stress intensity factors for crack initiation and for unstable crack growth were determined through incremental step load (ISL) and rising displacement (RD) testing coupled with the direct current potential difference (DCPD) method. Slow strain rate (SSR) tensile tests were also performed to evaluate hydrogen embrittlement susceptibility. Microstructures with no δ phase and three different strength levels and a microstructure with an intermediate strength level that contained δ phase were evaluated. For UNS N07718 microstructures without δ phase, the stress intensity factor for unstable crack growth increased with increasing yield strength and exhibited an inverse relationship with the total elongation ratio from the SSR tests. The presence of δ phase decreased the stress intensity factor for unstable crack growth but did not affect the stress intensity for crack initiation. Fracture modes were evaluated with scanning electron microscopy and were independent of testing method.

Key words: Precipitation hardened nickel-base alloys, Hydrogen embrittlement, Slow strain rate testing, Incremental step load testing, Rising displacement testing, UNS N07718

INTRODUCTION

UNS⁽¹⁾ N07718, commonly referred to as alloy 718, is one of several precipitation-hardened nickel-base corrosion resistant alloys (CRAs) used for components in deep sea oil wells. Ni-base CRAs are used for packers, tubing hangers, fasteners, valves, and bolting components in deep-sea oil wells because of their high-strength, high toughness, and corrosion resistance; however, field failures of these components have occurred due to hydrogen embrittlement.¹⁻³

Precipitation-hardened Ni-base CRAs are primarily strengthened by coherent and/or semi-coherent γ'' and γ' precipitates formed during aging. Thermomechanical processing and aging may also result in the formation of additional precipitates at grain boundaries, such as δ phase, and carbides within grains. It is well known that δ phase can increase the hydrogen embrittlement susceptibility of Ni-base CRAs by inducing hydrogen-affected intergranular and/or interphase cracking.^{1, 2, 4-6} API⁽²⁾ standard 6ACRA provides guidelines for annealing and aging heat treatments and acceptable mechanical properties of UNS N07718 and other Ni-base CRAs for use in downhole environments.⁷ In certain service conditions, UNS N07718 can experience hydrogen embrittlement despite being heat treated according to the API 6ACRA standard due at least in part to limited δ -phase precipitation along grain boundaries,^{2, 3} these precipitates are formed during the aging step of the heat treatment. The effect of the γ'' and γ' precipitates on hydrogen embrittlement in Ni-base CRAs when δ phase is not present is unclear, in part due to the difficulty of producing high strength microstructures with no δ phase.

Hydrogen embrittlement testing of Ni-base CRAs for oil and gas applications normally involves accelerated fracture mechanics testing of notched or pre-cracked specimens or slow strain rate (SSR) tensile testing of smooth specimens. These test methods are typically performed with *in situ* electrochemical hydrogen charging at or near room temperature. There is currently no standard guiding the hydrogen embrittlement environmental testing parameters for Ni-base CRAs in oil and gas environments. SSR testing of smooth specimens is frequently chosen to evaluate hydrogen embrittlement susceptibility of Ni-base CRAs due to the relatively short duration of the test (~2 days) and the simplicity of the testing setup.^{2, 4, 6, 8-18} The ratio of ductility measured from tests performed with *in situ* hydrogen charging to tests in an inert environment (total elongation, reduction of area, yield strength) are used to determine relative susceptibility to hydrogen embrittlement for those alloys in the testing environment.^{19, 20} A drawback of the SSR test is that crack initiation and propagation are not detected, and therefore, the results can only provide a relative comparison and cannot be used to generate design properties.

Accelerated fracture mechanics testing is commonly performed for HE evaluation because it is possible to determine fracture properties relevant for design purposes, and test durations are normally limited to a few days.²¹ The incremental step load (ISL) test attempts to simulate the constant load/displacement conditions experienced in service by incrementally increasing the load on the specimen and then holding at a constant displacement for a pre-determined amount of time. ASTM⁽³⁾ standard F1624 provides guidelines for determining the step sizes and step times for steels, but no standard exists for ISL testing of nickel-base alloys. As described in ASTM standard F1624,²² a decrease in load at an increasing rate during a constant displacement hold is assumed to indicate the onset of unstable fracture. However, it is unclear whether the load drop is sensitive to crack initiation and subsequent stable crack growth in these alloys. For high toughness alloys, it is possible that crack initiation and crack growth occur prior to the observed load drop. Rising displacement testing is another type of accelerated fracture mechanics test method and is essentially an SSR test of notched or pre-cracked specimens with an *in situ* method of determining the onset of crack growth, such as the direct current potential difference (DCPD) technique or measurement of the compliance of the specimen during the test.²³

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The DCPD technique allows for the measurement of very small cracks and is therefore useful in identifying crack initiation and measuring crack growth during fracture mechanics testing. In the DCPD technique, a constant direct current is passed along the length of the specimen, and the voltage across the notch of the specimen is measured. When a crack initiates and grows at the notch, the resistance across the notch increases due to the reduction in cross-sectional area, which results in an increase in the measured voltage. The change in crack size is calibrated to the change in output voltage.

Hydrogen embrittlement susceptibility is evaluated in this paper through incremental step load (ISL) and rising displacement (RD) testing of circular notch tensile (CNT) specimens and slow strain rate (SSR) tensile testing of smooth specimens with *in situ* cathodic hydrogen charging. The direct current potential drop (DCPD) technique is implemented in the ISL and RD test methods to provide a measurement of crack initiation and crack growth resistance. The ISL test combined with the DCPD technique was also used to determine the onset of unstable crack growth. The hydrogen embrittlement susceptibility of four UNS N07718 microstructures were evaluated: three microstructures with different strength levels and no δ phase and one microstructure with an intermediate strength level that contained δ phase. The hydrogen embrittlement susceptibilities produced in this study are evaluated with respect to the testing methods, microstructures, mechanical properties, and fracture modes.

EXPERIMENTAL PROCEDURES

UNS N07718 with the composition given in Table 1 was hot-rolled to a plate with a thickness of 1.91 cm (0.75 in) and a width of approximately 23 cm (9 in). The plate was sectioned, then annealed and aged in box furnaces according to the heat treatments in Table 2. Annealing was performed with the highest allowed time and temperature within the guidelines of API standard 6ACRA (1050 °C for 2.5 h) to ensure complete dissolution of δ phase produced during the previous thermomechanical processing and a consistent grain size and was followed by water quenching. Grain sizes for each heat treatment were determined with the concentric circles method outlined in ASTM standard E112.²⁴ All microstructures exhibited a grain size between 128-143 μm .

Table 1
Composition of Nickel-Base Corrosion Resistant UNS N07718

wt %	Ni	Cr	Nb	Mo	Ti	Al	Co
UNS N07718	53.39	18.44	5.00	2.87	1.02	0.52	0.33
C	Mn	Si	P	S	B	Cu	Fe
0.015	0.119	0.075	0.009	0.0004	0.003	0.10	17.99

For the under-aged 710, double-aged, and under-aged 680 microstructures, aging was performed at lower temperatures (720 °C or less) to avoid grain boundary δ phase precipitation and to produce microstructures with a range of strength levels. The peak-aged microstructure in Table 2 was produced with the lowest aging temperature and time allowed in API standard 6ACRA, which has been shown to result in a small amount of grain boundary δ phase.⁷ For all single step aging treatments in Table 2, the plates were air cooled after aging. For the double-aged microstructure (720 °C for 8 h, 620 °C for 8 h), the plates were water quenched after the first aging step and air cooled after the second aging step. To determine if δ phase was present at the grain boundaries, scanning electron microscopy (SEM) was conducted on a JEOL 7000[†] field emission scanning electron microscope (FESEM). The peak-aged microstructure was the only microstructure that contained grain boundary δ phase, and the δ phase could only be identified in the peak-aged microstructure with the FESEM at a magnification of 4000X or greater. Rockwell C hardness testing was performed according to ASTM E18.²⁵ Room temperature tensile tests were performed for each microstructure in air at an engineering strain rate of $5.0 \times 10^{-4} \text{ s}^{-1}$.

[†] Trade name.

Table 2
Annealing and Aging Temperatures and Times for UNS N07718

Designation	Annealing Temperature (°C)	Annealing Time (h)	Aging Temperature (°C)	Aging Time (h)
Under-aged 710	1050	2.5	710	6
Double-aged	1050	2.5	720+620	8+8
Under-aged 680	1050	2.5	680	140
Peak-aged	1050	2.5	760	6

ISL and RD tests with *in situ* hydrogen charging were conducted with circular notch tensile (CNT) specimens, which were machined with a major diameter of 12.7 mm (0.50 in) and a diameter at the notch of 8.00 mm (0.315 in). The notch radius of the CNT specimens was 0.086 mm (0.0034 in) or less resulting in a stress concentration factor (K_t) of 6 or greater.²⁶ The notch was turned down on a lathe, and the specimens were polished to a R_a surface finish of 0.254 μm (10 μin). CNT specimens of a comparable diameter with stress concentration factors of 6 or greater have been shown to produce fracture toughness values that are comparable to fracture toughness values from fatigue pre-cracked compact tension specimens.²⁷ Additional benefits of the CNT specimen are that a much smaller thickness can result in plane strain conditions than conventional compact tension specimens and the necessary experimental setup is simple.²⁷ Stress intensity factors were calculated for the CNT specimen geometry with Equation 1 where P is the applied load, d is the minor diameter of the specimen, a is the crack length, and F is a geometry factor that is dependent on the major diameter (D), d , and a .²⁸

$$K = \frac{P}{\pi(d-a)^2} \sqrt{\pi(d-a)} F \quad (1)$$

ISL testing with DCPD was performed with 2,670 N (600 lb) step sizes and 2 h step times. A displacement rate of $2.5 \times 10^{-3} \text{ mm} \cdot \text{s}^{-1}$ ($1 \times 10^{-4} \text{ in} \cdot \text{s}^{-1}$) was used to increase the load between the holds at constant displacement. For RD testing with DCPD, a crosshead displacement rate of $1.8 \times 10^{-5} \text{ mm} \cdot \text{s}^{-1}$ ($7.0 \times 10^{-7} \text{ in} \cdot \text{s}^{-1}$) was used. Due to the difference in displacement rates, about two-thirds as much time in the RD test was required to reach a given load as was required in the ISL test. Two ISL tests with DCPD were performed on each microstructure, and at least one test reached unstable crack growth for each microstructure. One RD test with DCPD was performed on each microstructure, and the tests were interrupted shortly after the peak load was reached.

Direct current of 2 A was applied along the length of the specimen. Two voltage probes were placed across the notch to measure the voltage across the notch and two additional probes were placed along the specimen away from the notch to provide a reference voltage. The effect of fluctuations in temperature and current were minimized by normalizing the notch voltage by the reference voltage (V/V_{Ref}). Voltage ratio measurements were recorded once every 10 s throughout the ISL and RD tests. For each test, the recorded voltage ratio (V/V_{Ref}) was normalized by the initial measured ratio ($V_0/V_{0-\text{Ref}}$), so that at the start of the test the ratio (V/V_0) is 1 and (V/V_0) increases with increasing crack length. This ratio (V/V_0) will be referred to as the normalized voltage ratio (NVR). The resistance associated with the reference voltage is assumed to not change significantly during the test.

In order to determine the relationship between the NVR and the crack length, several ISL and RD tests were interrupted before final failure, and the crack lengths were measured. A quadratic (2nd order polynomial) was fit to the crack length vs NVR data so that the crack length at any point in the ISL or RD test could be calculated based on the NVR.

The threshold stress intensity factor for crack initiation (K_{Ii}) was determined as the load at the inflection point where the voltage began to rapidly increase in the RD test. In the ISL test, a step was deemed to be the first step of stable crack growth when the average NVR for that step increased to 1.0005 or greater which equates to a crack size of 1.4 μm . To provide a conservative measure of K_{Ii} in the ISL

test, the load at the last step before crack initiation was used to calculate K_i . Crack initiation and stable crack growth occurred during the loading steps of the ISL test, and the constant voltage signal indicated that crack growth arrested during the hold periods. Unstable crack propagation was interpreted to occur when an increase in crack length (NVR) was detected throughout the constant displacement hold. As in determining K_i , the threshold stress intensity factor for unstable crack growth (K_{iu}) was calculated with the load and crack length at the last step of stable crack growth (a_u). In the RD test, the continuous increase in displacement does not allow the crack to arrest so K_{iu} cannot be determined. Additional information regarding the DCPD procedures for this study can be found elsewhere.⁵

Additional ISL tests without the DCPD technique were performed with a 4,450 N (1,000 lb) step size and 2 h and 4 h step times and with a 2,670 N (600 lb) step size and a 2 h step time. For ISL tests without DCPD, K_{th} was estimated based on the methodology outlined in ASTM F-1624: the onset of crack growth is assumed to be represented by a decrease in load at an increasing rate, and K_{th} is calculated based on the final load of the step before crack growth.²²

SSR testing was performed with smooth subsize tensile specimens with a gauge length of 25.4 mm (1.00 in), a gauge diameter of 3.81 mm (0.15 in), and a R_a surface finish of 0.254 μm (10 μin), as specified in NACE TM0198.¹⁹ A screw-driven Cortest[†] load frame with a load capacity of 44,500 N (10,000 lb) and a compliance of 22 MN/m was used for the SSR tests. Tests were performed with an engineering strain rate of $1.0 \times 10^{-6} \text{ s}^{-1}$, and displacement measurements were made with a linear variable differential transformer (LVDT) attached to the load frame. Three tests were performed in the ambient laboratory environment, and three tests were performed with cathodic polarization of the specimen for each microstructural condition. For all microstructural conditions, the ratios of the average yield stress, ultimate tensile stress, total elongation, and reduction in area from the cathodic polarization tests versus the ambient environment tests were calculated.

The same *in situ* environmental parameters and electrochemical cell design were used for all ISL, RD, and SSR tests. The electrolyte solution was 0.5 M H_2SO_4 , and the solution was deaerated with 99.9 % pure argon gas before the test began. The argon gas was also bubbled through the solution at a rate of 28 L/h (1 ft^3/h) to stir the solution throughout the test. Cathodic polarization was performed at a current density of 5 mA/cm^2 . Two iridium-tantalum oxide coated titanium mesh anodes functioned as the counter electrodes and were positioned on opposite sides of the specimen. Fracture surfaces from ISL, RD, and SSR testing were cleaned with methanol. Secondary electron imaging of the fracture surfaces was performed on the FESEM with an accelerating voltage of 20 kV and a working distance of 15 mm.

RESULTS AND DISCUSSION

The Rockwell C hardness and room temperature tensile results for all microstructural conditions of UNS N07718 are provided in Table 3. For the microstructures with no grain boundary δ phase, the yield stress, UTS and hardness increased, and the total elongation decreased from under-aged 710 to double-aged to under-aged 680. The peak-aged microstructure that contained δ phase exhibited intermediate yield stress, UTS, and elongation properties.

Table 3
Hardness and Tensile Properties of UNS N07718 Microstructures

Designation	Hardness (HRC)	0.2% Yield Stress (MPa)	UTS (MPa)	Total Elongation (%)
Under-aged 710	30.2±0.7	718±5	1053±6	48±2
Double-aged	39.0±0.4	938±4	1182±8	35±2
Under-aged 680	41.6±0.4	1094±9	1263±14	27±0
Peak-aged	39.0±0.4	989±0	1256±6	30±2

[†] Trade name.