

The Effect of Interactions between Cathodic Protection Potential and Stress Concentration on Hydrogen Embrittlement of Precipitation-Hardened Nickel Alloys

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ABSTRACT

Precipitation-hardened nickel alloys (PHNAs) are widely used for demanding oil and gas subsea applications, because of their high strength and corrosion resistance. However, several failures were associated with hydrogen embrittlement, under cathodic protection (CP), as subsea CP systems can provide a source of atomic hydrogen, which can diffuse into the material and compromise its toughness. The risk of hydrogen embrittlement might be reduced if CP systems were appropriately designed, e.g. more positive CP potentials could locally be applied to CRA components. Whilst tailored CP profiles will remain a practical challenge, the relationship between the CP potential and localised loading, due to the presence of stress raisers, is yet to be established.

This paper aims to address whether there is a threshold potential, above which embrittlement will not occur, and whether this threshold will be a function of stress intensity/concentration factor. This was explored through conducting slow strain rate tensile (SSRT) and incremental step load (ISL) testing on UNS⁽¹⁾ N07716, which has previously been associated with failures, at potentials between -750 and -1050mV_{Ag/AgCl}, on plain-sided specimens. Additional fracture-toughness-based testing, using single edge notch bend (SENB) specimens, was undertaken to understand if the stress intensity (associated with a fatigue pre-crack), can increase susceptibility to embrittlement.

Key words: UNS N07716, Hydrogen embrittlement, Slow strain rate testing, Incremental step load testing, ASTM E1820

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

INTRODUCTION

Precipitation hardened nickel alloys are commonly used in demanding and aggressive environments where a combination of high strength and corrosion resistance is required. They are therefore frequently selected for applications requiring high strength in downhole, wellhead, subsea and Christmas tree applications¹. The microstructure of all PHNAs consist of a primary austenitic (γ) phase, which is solid solution strengthened by alloying elements, such as Cr, Mo and Ti. UNS N07716, includes additions of Nb and Ti and is therefore also strengthened by γ' ($\text{Ni}_3\text{Al/Ti}$) and γ'' (Ni_3Nb) precipitates, which are dispersed through the matrix². The microstructure of PHNAs can also include the non-strengthening and deleterious δ and laves phases, and various metal carbides.

Despite having good resistance to sulphide stress cracking and stress corrosion cracking, PHNAs are known to be susceptible to hydrogen embrittlement under the combined influence of sufficiently high stress and atomic hydrogen content, and a susceptible microstructure. Early failures of the PHNA Alloy 718 had led to guidance, stipulated in API⁽²⁾ 6A718³, which specified a restricted chemistry to ensure limited δ phase formation, and specified that secondary phases not be distributed continuously or semi-continuously along grain boundaries. This microstructural guidance was applied to newer, more corrosion resistant grades, such as UNS N07716, in API 6ACRA⁴, but failures have not been prevented despite materials meeting API 6ACRA specifications⁵. This has led to suggestions that API 6ACRA include more extensive quality assurance/quality control (QA/QC) requirements, for materials other than Alloy 718, with a specified minimum yield strength of 120ksi, for which the Standard was originally developed¹. The exact form of any new QA/QC requirements is still unknown; however, the utility of microstructural guidance is in question as features of importance are only visible with high resolution microscopy, which limits the examination of large areas and can therefore be unrepresentative. Using unquantified data, such as images, is also subjective, whilst for materials other than Alloy 718 (120K) the correlation between microstructural features, at any scale, and failure has not been established.

Although microstructures are important considerations for assessing and mitigating the risks of hydrogen embrittlement, it is also suggested that the susceptibility can be controlled by modification of CP potentials, i.e. by making the environment more benign. The purpose of this paper was therefore to explore whether there was a threshold level of CP, above which hydrogen embrittlement did not occur, in UNS N07716. This alloy was chosen because it is an alloy in API 6ACRA that had been associated with previous failures⁶, whilst it also represents a worst case scenario as the alloy is thought to be more brittle under CP than other alloys⁷. This investigation was intended to demonstrate the initial feasibility of such an approach and therefore does not address aspects such as the influence of complex geometries, the influence of current density as opposed to potential and the influence of other sources of hydrogen, e.g. internal hydrogen.

SSRT and ISL testing was undertaken on plain-sided specimens, whilst additional fracture testing, on SENB specimens, was conducted to gain further insight into whether a stress threshold, established on plain-sided specimens, was still applicable in the presence of a stress raiser, such as a fatigue pre-crack. This is an important consideration as PHNAs are often used for high strength fasteners, where the threads act as stress raisers. Recent research on alloy steels have revealed a significant influence of stress intensity on environmental crack growth rates⁸.

(2) American Petroleum Institute (API), Washington, DC.

EXPERIMENTAL PROCEDURE

Materials and Microstructural Characterisation

Characterisation and testing was undertaken on forged UNS N07716 material. The chemical composition of the material was determined quantitatively, using optical emission spectrometry (OES). Metallographic cross-sections were prepared from the forging and examined, in the un-etched condition, using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Examination was also undertaken after etching in Kallings II solution, using light microscopy.

Post-test fractography was undertaken using light microscopy and SEM, with a particular focus on the extent of brittle fracture and the correlation of fracture morphology with mechanical test data.

Conventional tensile and hardness testing

Conventional tensile tests, in accordance with ISO⁽³⁾ 6892-1:2016, were undertaken, using round specimens, at ambient temperature in air, whilst Vickers hardness tests were undertaken with a load of 10kg. Mechanical test results were used to determine if the material conformed to the requirements of API 6A CRA.

Slow strain rate testing

SSRT was undertaken, in tension, at a nominal strain rate of $5.7 \times 10^{-6} \text{s}^{-1}$ ($1.3 \times 10^{-4} \text{mm/sec}$), at 4°C in 3.5% NaCl solution. Testing was undertaken at four CP potentials: -750, -850, -950 and -1050 mV_{Ag/AgCl}, whilst a singular specimen was also tested in air. Specimens were not pre-charged with hydrogen before testing. The cylindrical plain-sided test specimens had a nominal gauge length of 22.50mm, gauge diameter of 6.35mm and M8 threaded ends.

Incremental step load testing

The ISL testing methodology was based on ASTM⁽⁴⁾ F1624-12b, but tests were conducted in load control, rather than displacement control. The load profile consisted of 10 steps of 5% UTS increments, held for 2hrs per step, followed by 10 steps at 5%UTS increments, held for 4hrs per step. The UTS was determined based on conventional tensile test results. Testing was undertaken at 4°C in 3.5% NaCl solution, and under conditions of No CP, -750, -850, -950 and -1050 mV_{Ag/AgCl}. Specimens were not pre-charged before testing, and were of the same geometry as for SSRT.

Fracture testing

15x15x90mm SENB specimens were extracted and tested, in unloading compliance, in accordance with ASTM E1820. Samples were fatigue pre-cracked with initial and final loads of 6.00kN and 4.00kN, respectively, and an R ratio of 0.1. The crack length to specimen width ratio, a/w, was nominally 0.5.

Environmental fracture testing was undertaken at an initial K-rate of $0.005 \text{ Nmm}^{-3/2}/\text{sec}$ and a clip increment (to 'trigger' an unloading) of 0.01mm was used. In order to determine the machine displacement rate, to achieve this k-rate, the loading rate was calculated, using linear elastic fracture mechanics, the compliance of the entire test set-up (specimen in machine) was measured in the elastic regime, and with this information the required machine displacement rate, commensurate with the target K-rate, was finally calculated. Tests were undertaken at 4°C in 3.5% NaCl solution under conditions of No CP, -750 and -600mV_{Ag/AgCl}. Additional tests were also undertaken, without CP, in demineralised (DM) water, at 4°C and in air at ambient temperature.

⁽³⁾ International Organization for Standardization (ISO), Geneva, Switzerland.

⁽⁴⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

RESULTS

Materials and Microstructural Characterisation

The composition of the UNS N07716 material is detailed in Table 1, and mainly conformed to the requirements of API 6ACRA, although the level of Ti was slightly higher than the specified range.

Table 1 Parent material chemical analysis results*. Values in red are outside the limits of API 6ACRA.

Sample	C	Si	Mn	P	S	Cr	Mo	Fe	Al	Cu	Nb
Parent	0.017	0.15	0.07	0.007	0.006	21.4	8.1	4.42	0.23	0.04	3.52
API 6ACRA UNS N07716	0.030 Max	0.20 Max	0.20 Max	0.015 Max	0.010 Max	19.0- 22.0	7.00- 9.50	Balance	0.35 Max	0.23 Max	2.75- 4.00
Sample	Ti		B**		Pb***		Ni by diff				
Parent	1.71		0.003		<0.01		60.2				
API 6ACRA UNS N07716	1.00-1.60		0.006 Max		0.001 Max		59.0-63.0				

* TWI Report Number: S/19/2

** Not on UKAS schedule

*** Detection limits larger than limits in standard

Max: Maximum

Min: Minimum

diff: Difference.

Microscopic images of the UNS N07716 material are shown in Figure 1. The grain structure was equiaxed with an apparent semi-continuous distribution of precipitates along grain boundaries. Acicular precipitates were not evident along grain boundaries. Back-scatter SEM images of the microstructure, in the unetched condition, are shown in Figure 1c and 1d, with only a very limited amount of grain boundary precipitates observed. TEM imaging, Figure 1e, also suggested a semi-continuous distribution of grain boundary precipitates, and EDX analysis of the precipitates revealed that they were Mo and Ti rich, relative to the matrix, suggesting they were MC type titanium carbides. Further analysis to determine precipitate size and distribution was not undertaken, primarily because the precipitates were only clearly visible using TEM, which does not lend itself to analysis of the large areas necessary to determine these characteristics. The grain size was determined to be ASTM No. 4, using light microscopic images and ASTM E112 grain size comparison charts.

Conventional tensile testing and hardness testing

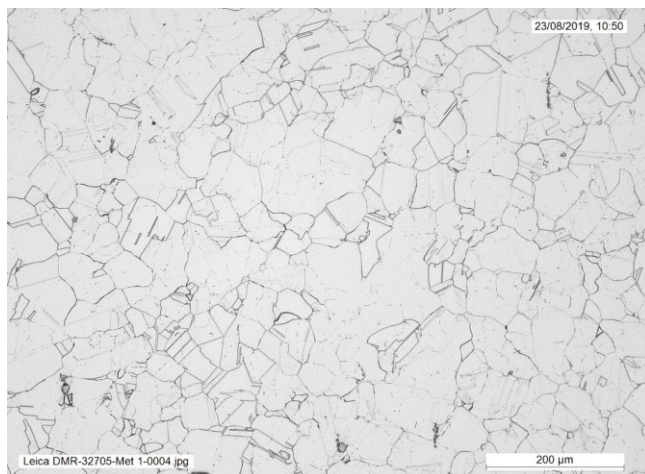
Room temperature tensile test results are included in Table 2, whilst hardness test results are given in Table 3. Tensile test results showed conformance to the requirements of API 6ACRA, and the average hardness of five indents (42.9 HRC), was just below the maximum specified, for the material in question, in API 6ACRA (43 HRC).

Table 2 Room temperature tensile test results*.

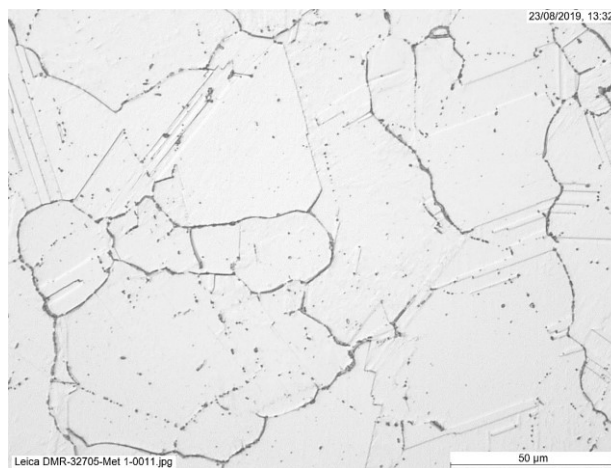
Specimen	0.2% Proof Strength (MPa)	Ultimate Tensile Strength (MPa)	Elongation (%)	Reduction in Area (%)
T90021 Mk1	1093	1386	30.0	39
T90021 Mk2	1105	1403	32.0	36
T90021 Mk3	1097	1396	32.0	36
API 6ACRA UNS N07716 (140K)	965-1103	1138 Min	18 Min	20 Min

* TTH Reference number: T90021.

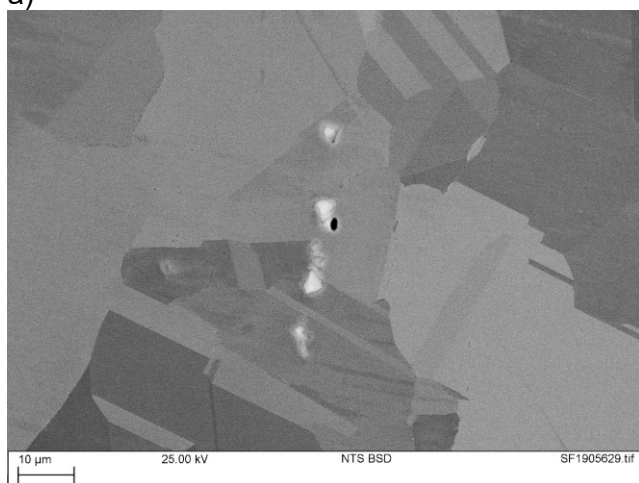
Min: minimum.



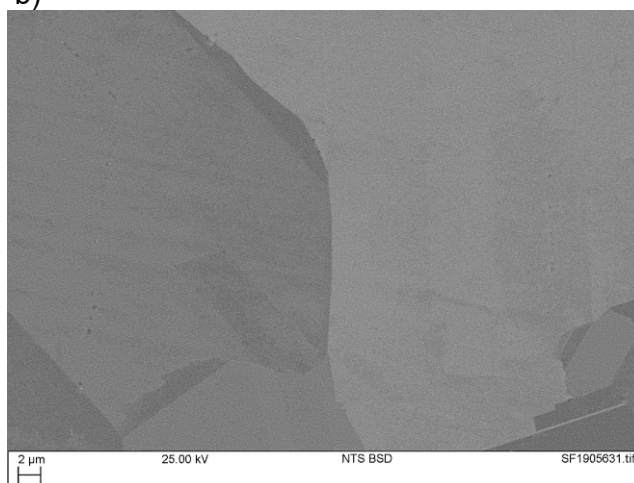
a)



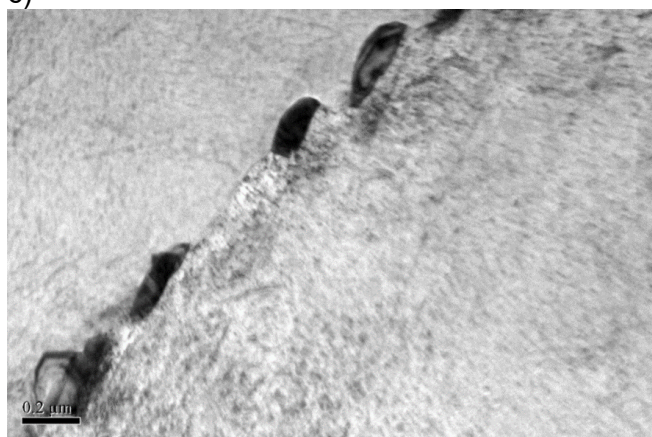
b)



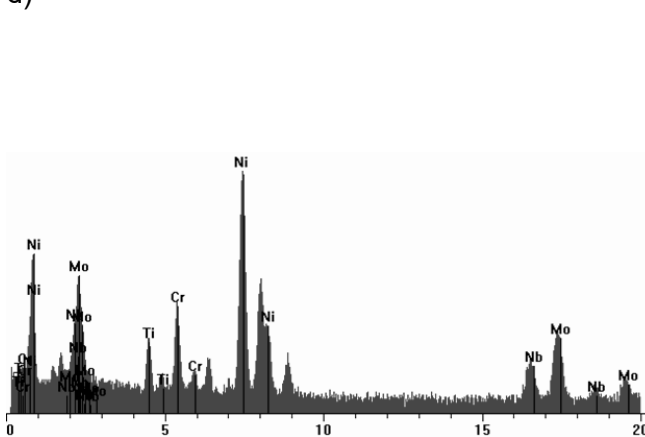
c)



d)



e)



f)

Figure 1 Light microscopy, SEM and TEM images of the microstructure:

- a) Low magnification image after etching in Kallings II solution;
- b) High magnification after etching in Kallings II solution;
- c) Back-scatter SEM image in the unetched condition, with a nominal magnification scale;
- d) Back-scatter SEM image of a grain boundary, with a nominal magnification scale;
- e) TEM image of a grain boundary;
- f) Spot TEM EDX analysis from a grain boundary precipitate.