

Paper No.
16709



Hydrogen Stress Cracking Resistance of High Strength Alloys for Subsea Fasteners

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ABSTRACT

Sacrificial aluminum-indium anode cathodic protection is commonly used for protecting offshore and subsea structures. As a consequence, all metallic fasteners are hydrogen charged under high tensile stresses at the thread roots. This means that material selection must prevent the occurrence of hydrogen stress cracking (HSC) under these conditions. For most equipment where low strength fasteners are sufficient a low alloy steel can be used provided a maximum yield strength and hardness are specified. When higher strength fasteners are required, low alloy steels must be replaced by corrosion resistant alloys which must be qualified with regard to their susceptibility to HSC. In this work, precipitation-hardened nickel alloys from API 6ACRA, work hardened austenitic stainless steels and nickel alloys with yield strengths up to 200 ksi (1240 MPa) have been tested under cathodic protection using a specific test methodology. The objective was to quantify their resistance to HSC and identify their limits of use when exposed to cathodic protection. The results are presented and discussed in the light of current knowledge on HSC for subsea fastener applications.

Key words: Hydrogen Stress Cracking, nickel alloys, PH nickel alloys, Oil and Gas, cold work

INTRODUCTION

Bolted connections for subsea flanges and other components must be reliable as they are often used for pressure containing components (subsea Christmas trees, connectors ...). When possible, the primary choice for bolting is low-alloy steel with a limitation of actual yield strength (135 ksi) and a maximum hardness of 34 HRC to prevent HSC. In some cases, the use of low-alloy steel is prohibited and corrosion resistant alloys (CRAs) must be used. This is the case when higher strength is required and also for sour service resistance under thermal insulation. In addition, CRAs do not require temporary corrosion protection coatings.

There is limited literature dealing with high strength subsea fasteners. Eskalul et al. listed possible alloys for use as subsea fasteners with yield strength above 150 ksi. Among these they highlighted alloys with good resistance to environment-assisted cracking (EAC) including some martensitic stainless steels (SS), precipitation-hardened (PH) nickel alloys and cobalt alloys.^{1,2}

This list of alloys was based on EAC resistance including stress corrosion cracking (SCC) in seawater, sustained load cracking (SLC and hydrogen stress cracking (HSC)) in seawater under cathodic protection.

In this work focus has been put on HSC for selecting the best alloys for high strength subsea fasteners when exposed to cathodic protection.

Industry experience indicates that martensitic SS are not the best candidates for subsea fasteners because they are quite sensitive to HSC. Cobalt alloys are not the primary choice unless very high strength is needed. We are then essentially left with nickel-based alloys and stainless steels.

Today in API 6ACRA only two PH nickel alloys have a 150 ksi specified minimum yield strength (SMYS): UNS N07718 and UNS N09946. Some cold worked alloys are also possible candidates as shown by several manufacturers data for N06686, N06059 and N07022.^{3,4,5} Some selected austenitic SS can be cold worked to reach a 150 ksi yield strength with an expected good resistance to HSC.

For lower strength fasteners (below 150 ksi) PH nickel alloys can be used but they do not all have the same resistance to HSC as demonstrated by a large study performed on many heats.^{6,7} The most resistant alloys were γ' alloys like UNS N09925. UNS N07718 and UNS N09945 had a good HSC resistance. UNS N09946 had a more scattered HSC resistance while UNS07725 and UNS07716 were the least resistant. These results were obtained with slow strain rate under severe hydrogen charging conditions. The test procedure used in this study is now published as an Appendix C of NACE TM0198 Standard. Note that this type of test may be used as a material acceptance test for HSC resistance. In no way it is meant to simulate service conditions.

Among lower strength stainless steels, duplex SS are not considered a reliable option when exposed to cathodic protection as they need to be in compliance with DNV RP F112 to prevent HSC.⁸ Other alloys like UNS S66286 have shown good HSC resistance as well as some cold worked highly alloyed austenitic stainless steels.⁹⁻¹¹

Based on the above discussion, Table 1 lists the alloys selected for high strength subsea fasteners. In this Table the crevice corrosion resistance is also listed because for some applications cathodic protection cannot always be guaranteed. In such a case, some alloys may not be acceptable because of their poor crevice corrosion resistance in seawater.

The slow strain rate technique has been used to assess material resistance to HSC for qualification. It is recognized however that it is not fully quantitative and is not a fit for purpose test. This technique is used to compare materials performance and assess heat to heat variability regarding alloy resistance to HSC.

The aim of the present work was to rank alloys as regard to their HSC resistance for subsea applications using standard cathodic protection. Since these materials were for use as subsea fasteners the objective was to quantify their HSC resistance under constant load simulating the local plasticity present at thread roots.

This paper summarizes the results obtained to date. It attempts to identify the most HSC resistant high strength materials for subsea fasteners when exposed to cathodic protection. It is meant to quantify their relative resistance to HSC.

EXPERIMENTAL

Materials

The tested materials were selected from those listed in Table 1 because they are common alloys in the Oil and Gas industry and/or they represent potential candidates for high strength subsea fasteners. The selected PH nickel alloys are listed in API⁽¹⁾ 6ACRA: 120K, 140K and 150K UNS⁽²⁾ N07718, UNS N09925, UNS N07725 and UNS N09946. Cold worked Ni-Cr-Mo alloys are UNS N06625 (10%), UNS N01276 with two cold-work levels (30% and 44%), UNS N07702 in the cold-worked (44 and 50%) condition and, cold worked (44%) and aged condition. UNS N06625 was also tested annealed. Precipitation-hardened martensitic stainless steel UNS S17400 was included for reference in two ASTM⁽³⁾ 1 listed heat treated conditions: H900 and H1150M. Austenitic stainless steels, either precipitation hardened UNS S66286 or cold worked (25%) UNS S31010 and (~30%) UNS S31266. Chemical compositions and tensile test results are indicated in Tables 2 to 5 for the two series of materials tested as studs and notched tensile specimens, respectively.

Materials were obtained from manufacturers in the form of bars with diameters mostly ranging between $\frac{3}{4}$ (19.05 mm) and 2.5 inches (63.5 mm). Two alloys were machined in larger diameter forgings. Diameters are given in Tables 3 and 5. The test specimens were either rolled for studs or machined for notched specimens. Their microstructure was characterized by optical microscopy and scanning electron microscopy (SEM). Observations of microstructures were performed on cross sections. SEM was used to detect small precipitation and characterize microstructure with higher resolution. Energy dispersive X-Ray spectroscopy (EDX) was used to evaluate the composition of precipitates when required. Alloys were commercial alloys supplied to API 6ACRA or ASTM standards. Alloys were characterized in terms of chemistry, mechanical properties and microstructures. Some examples of PH nickel alloy microstructures are shown in Figure 1. UNS N07718 and UNS N09946 microstructures appear to be free of continuous grain boundary precipitation. In the case of UNS N07725 grain boundaries are clearly revealed optically by etching. Very fine precipitates (about 0.5 μm) are only observed at high magnification in the SEM at some grain boundaries as shown in Figure 1.i.

Specimens and loading

This work focuses on threads where subsea fastener failures have been experienced. The testing of smooth specimens is not representative of threaded components and much less detrimental. Experience indicates that hydrogen stress cracks in austenitic alloys occur at thread roots where plastic strain is localized plain stress conditions prevail.

⁽¹⁾ American Petroleum Institute, Washington, DC

⁽²⁾ Unified Numbering System for Metals

⁽³⁾ American Society for Testing and Materials, West Conshohocken, PA

The tensile load is applied based on a percentage of actual measured yield strength (AYS). However, in thread roots it is recognized that the material is stressed above yield.

In the first series of tests a number of materials were tested as 10 mm diameter studs under dead weight loading in natural seawater at 5°C and polarized at -1.1 V vs Ag/AgCl to simulate cathodic protection. High strength nickel alloys and stainless steels were selected as potential candidates for fasteners. Threads were rolled, not machined. Table 1 shows the materials and their properties. Incremental loading was applied with an initial stress equal to 90% AYS for 3 months. After this period scanning electron microscopy (SEM) examination of the thread root area was used to confirm for any evidence of cracking. Then, the stress was incremented by 2% every week until failure. Failure was detected by a load drop or SEM examination when no load decrease occurred.

After the screening phase a simplified approach was adopted to test material threads. A 6.35 mm (1/4 inch) cylindrical reduced NACE specimen with a circular notch was used. The notch geometry was defined using finite element analysis (FEA) to obtain a stress/strain distribution in the notch equivalent to a root thread with a stress concentration factor (K_t) in the expected range between 3 and 5. Figure 2 shows an example of FEA. The notch was machined to obtain a K_t of 4.5. The specimen was immersed in a circulating 5% sodium chloride solution. Specimens were connected to an aluminum-Indium sacrificial anode to simulate subsea cathodic protection. The potential was checked and recorded every working day. Specimens were loaded with a large proof ring typically used for constant load testing of NACE specimens. An incremental step loading (ISL) technique was used.

Incremental load testing

The loading steps were based on the mechanical properties of the tested alloys. For the notched specimens, it was assumed that the load to failure (or maximum load F_{max}) corresponded to the ultimate tensile strength (UTS) of the alloy, which is the conventional approach for bolting. Then, the elastic load was calculated using the YS/UTS ratio from F_{max} .

The test method is illustrated in Figure 3. A first specimen was tested starting from 100% of the YS. Steps of 2% YS, three times a week, were used until failure of the sample. If failure occurred within 10 days, an additional sample was tested at lower load, 10% lower than the failure load. This decrease of the initial load was repeated until the test lasted at least 10 days. Then, the next two samples were tested successively at 93% of the failure load of the previous sample (rounded to the nearest integer) with step load of 1% of YS. In case of scattering of the results, an additional sample was tested to have at least 2 samples that failed at a same load level (+/-1%). The threshold was defined as the maximum level reached without failure. This way, the accuracy of the threshold should be in the range of 1% of YS.

A last sample was tested starting 5% below the stress threshold and using 1% load steps. A crack monitoring system using acoustic emission (AE) was used to detect crack initiation. This technique is based on the detection of elastic transient waves released by the tested specimen during crack initiation and propagation using piezo-electric sensors coupled to the specimens. The AE detection system used during this study was composed of a 2-channels PCI2 acquisition system with two resonant sensors R15D.

At the end of the tests, fracture surfaces were investigated by SEM to assess the extent of brittle area, linked to the sensitivity of the alloy to hydrogen embrittlement. The morphology of the fracture gave information about the embrittlement mechanism. For instance, intergranular brittle fracture evidenced the effect of grain boundary precipitates whereas transgranular brittle fracture was related to hydrogen-dislocation/intragranular precipitates interactions.

Constant load testing

For the validation of the stress threshold, constant load tests were performed under the same environmental conditions as incremental step load testing. Notched specimens were exposed at the stress threshold and above (+ 2%YS) for 1 month. At the end of the exposure, the notch root of unfailed samples was inspected with SEM. Three replicates were used per alloy and per stress level.

Acoustic emission was used to detect cracks under constant load. Successive load steps were performed until crack initiation started and propagation was observed. This technique allowed to better understand the cracking behavior of alloys with different HSC resistance: UNS N00925, UNS N07718, UNS N09946 and UNS N07725.

RESULTS

The results of the initial screening study on studs are presented in Figure 4. They are plotted as a percentage of AYS and UTS. This is particularly relevant because the applied maximum stress for subsea bolts and studs is 83% of the specified minimum yield strength (SMYS) from API Specification 17D/ ISO 13628-4. In this work we compare alloy resistance using %AYS knowing that there is an additional safety margin when using %SMYS. The 100% and 83% AYS lines have been drawn to help compare the alloys resistance to HSC. Arrows indicate that either they did not fail at all (UNS S66286 and 44%CW UNS N07022 and aged) or that they started to fail at 5 ksi (44%CW UNS N07022, 44%CW UNS N01276 and UNS N07718) above the stress indicated on the bar graph.

Alloys with very different strengths can be compared on a single plot giving a good indication of their HSC resistance under CP. Two alloys stand out for their excellent resistance: UNS N07022 CW and aged and UNS S66286 which is known to have excellent HSC resistance. Note, however, that these alloys have very different strengths with AYS of 206 ksi (1422 MPa) and 103 ksi (767 MPa), respectively. Then UNS N07022 CW is also quite resistant and just below UNS S17400 with the doubled ageing HT reach about 100%AYS. However, again, the nickel alloy has a very high strength approximately double compared to the low strength UNS S17400, 205 ksi (1413 MPa) versus 105 ksi (724 MPa). The results suggest that the ageing treatment improves significantly the HSC resistance of the CW UNS N07022. The other alloys, CW UNS N01276 and 120K UNS N07718 have an apparent comparable HSC resistance but again their AYS is very different. The CW UNS N01276 alloy has a much higher strength than UNS N07718 with 172 ksi (1185 MPa) versus 137 ksi (946 MPa), respectively. The arrow indicates that the HSC threshold is close to 100% AYS with a failure well above yield and no failure at 95%AYS. As expected, the UNS S17400 martensitic SS with the H900 low ageing treatment has a significantly lower HSC resistance.

In the same way as for studs, Figure 5 shows the results of HSC tests using notched specimen with the described ISL method. For this part the tested materials were essentially nickel alloys (mostly PH or CW) and stainless steels, UNS S66286 in the standard aged condition and 25%CW UNS S31010. As for the screening tests on studs, the results are presented as a percentage of AYS. As for studs, UNS S66286 and UNS N09925 stand out with an excellent HSC resistance. They both fail well above their macroscopic yield. Annealed UNS N06625 is also very resistant to HSC, but it has a much lower AYS compared to the two other alloys. When 10% cold worked with an AYS of 136 ksi (938 MPa), double its annealed AYS, it fails just above yield. A comparable HSC resistance is observed on all UNS N07718 alloys with strength between 120K and 150K. Cold worked (30%) UNS N01276 fails above yield also showing a good resistance to HSC. Cold worked austenitic SS UNS S31266 has a comparable AYS of 150 ksi (1034 MPa) and fails at a somewhat lower stress. Both CW austenitic SS UNS S31010 and UNS S32266 have similar HSC susceptibility with very close AYS.

The alloys with the lowest HSC performance are two PH nickel alloys: UNS N09946 and UNS N07725. UNS N09946 has a somewhat lower HSC resistance versus AYS than the 150 ksi above mentioned