

Evaluation of the hydrogen diffusion and transport kinetics in ASTM A508 grade 4N

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ABSTRACT

Low Alloy steels (LASs) are, by volume, the most widely used alloy family in critical oil & gas (O&G) components. However, the strength and hardness of LASs for sour environments are limited to prevent different forms of hydrogen embrittlement, such as hydrogen stress cracking (HSC) and sulfide stress cracking (SSC). Moreover, ISO 15156-2 (1) restricts LASs to a maximum of 1 wt% Ni due to SSC concerns.

In the present work, the hydrogen diffusivity of the nuclear-grade ASTM(2) A508 Gr.4N LAS was measured using the hydrogen permeation method. Results are linked to quenched and tempered (Q&T) microstructure features characterized by transmission electron microscopy (TEM). Additionally, a comparison was made between the A508 Gr.4N and a ferritic-pearlitic steel with similar Ni content. This work is connected with the HSC evaluation of the same alloy by slow strain rate testing (SSRT) described in a separate publication.

Key words: High-strength low alloy steel, hydrogen embrittlement, hydrogen stress cracking, environmentally assisted cracking, oil and gas, subsea, hydrogen permeation test, cathodic protection.

INTRODUCTION

Material requirements for unconventional Oil and Gas environments

Due to the progressive depletion of conventional oil and gas (O&G) reserves, the energy demand drifts its attention to unconventional reservoirs.¹ These new O&G fields pose challenges to the materials used that are often associated with high-pressure (>103 MPa) and high temperature (>177 °C) or, in arctic service, temperatures as low as -60°C.¹⁻³ Moreover, the presence of atomic hydrogen produced either from corrosion reactions or by cathodic protection can lead to hydrogen stress cracking (HSC). In sour environments, the cracking mechanism is referred to as sulfide stress cracking (SSC) in which H₂S acts as a hydrogen recombination poison and increases severity. Materials susceptible to hydrogen embrittlement (HE)—by either HSC or SSC—characterized by

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ductile behavior under normal circumstances, can fracture in a brittle mode in the presence of atomic hydrogen. Therefore, materials selection is paramount to reduce possible catastrophic failures.

Use of high strength low alloy steels for sour service applications

Low alloy steels (LASs) are widely used because of their low cost and good mechanical properties.¹ By appropriate heat treatment processing, a high yield strength (e.g., 690 MPa (100 ksi)) can be achieved while retaining adequate toughness. The hardenability can be enhanced by the addition of alloying elements such as molybdenum, chromium, and nickel.⁴

Nickel additions produce an increase in yield strength (YS) due to solid solution strengthening and subgrain size reduction.^{1, 5} Hardenability is improved with Ni as it stabilizes the austenite phase, delaying the austenite to martensite transformation.¹ Additionally, Ni increases the low-temperature fracture toughness due to grain refinement and modification of the ferrite properties.⁶ Furthermore, Ni has a low impact on weldability as reflected by its carbon equivalent coefficient, which is the lowest compared with other alloying elements.¹

Despite the beneficial effects of Ni, its content cannot exceed 1%wt when used in H₂S-bearing environments. In this regard, ISO 15156-2⁷ restricts the nickel content in LAS based on the assumption that higher Ni concentrations affect SSC resistance. This restriction was based on a body of research⁸ conducted during the 1960s, which was later disputed,^{9, 10} and remains controversial.¹ As reviewed by Kappes et al.,¹ microstructure determines the SSC resistance of LASs irrespective of their nickel content. For instance, Snape¹¹ improved the strength and SSC resistance of AISI 4340 (a LAS with Ni >1%wt) by tailoring the final steel microstructure.

Microstructural features and their effect on HE

As discussed by Depover et al.,¹² microstructural features influence the HE resistance of LASs. In this regard, Nagao et al.¹³ investigated the influence of carbide formers due to their potential beneficial effect on the HSC resistance of LASs. According to this work, carbides acted as traps reducing the amount of diffusible hydrogen, which is thought to play a detrimental role in hydrogen embrittlement. The trapping capacity of chromium carbides was quantified by Depover et al.¹⁴ using thermal desorption spectroscopy (TDS), slow strain rate testing (SSRT), and hydrogen permeation tests. The work indicated the beneficial effect of small M₂₃C₆ carbides (less than 100 nm) as they acted as hydrogen traps hindering hydrogen diffusion. The effect of molybdenum additions on HSC performance was studied by Hinotani et al.¹⁵ on medium carbon steel with 3.9%wt. Mo. The authors used a tempering stage to precipitate Mo₂C and evaluated its effect on hydrogen diffusion. It was concluded that after tempering, the fine Mo₂C carbides decreased the hydrogen diffusivity abruptly. The addition of vanadium as a carbide former was evaluated by Lee et al.¹⁶ on tempered martensitic steels with and without V. It was concluded that those steels with V additions trapped more hydrogen and were more resistant to HE than the V-free baseline steels.

ASTM A508 Gr.4N – a Ni-Cr-Mo low alloy pressure vessel steel and a promising candidate for subsea equipment in sour environments

Because of its improved strength, hardenability, and outstanding toughness, the ASTM A508 Gr.4N could be an excellent candidate for demanding O&G components. The chemical composition, mechanical properties, and manufacturing processes of this Ni-Cr-Mo high-strength LAS are specified in the ASTM A508/A508M Standard.¹⁷ The ASTM A508 Gr.4N is a nuclear-grade alloy that has high Ni (i.e., 2.8-3.9wt%) and a specified minimum yield strength (SMYS) of 690 MPa (100 ksi). Due to its high strength and high fracture toughness, the A508 Gr.4N has been proposed for reactor pressure vessel applications (RPV).^{5, 18} The quenched and tempered (Q&T) A508 Gr.4N alloy has a microstructure composed of lower bainite and tempered martensite, which can be obtained uniformly throughout thick sections.⁵

In previous work, Viereckl et al.¹⁹ estimated the HSC resistance of the nuclear-grade ASTM A508 Gr.4N alloy using SSRT as a function of applied cathodic potential. The HSC resistance of the A508 Gr.4N alloy was compared against the results obtained by Husby et al.²⁰ on a ferritic-pearlitic LAS

with similar Ni content (3 %wt.) but a lower YS of 320 MPa (46 ksi). The SSRT ratios demonstrated that with more severe charging environments, the A508 Gr.4N had better resistance to HE than the 3 wt.% Ni steel from Husby et al.²⁰ However, limited information is available in the open literature on the hydrogen permeation kinetics of A508 Gr.4N.

The objective of this work is, thus, to quantify the hydrogen transport kinetics of A508 Gr.4N. As a continuation of the characterization made by Viereckl et al.,¹⁹ this paper will expand our understanding of the HE resistance of this material.

EXPERIMENTAL PROCEDURE

Materials

As described previously,¹⁹ forged ASTM A508 Gr.4N plates were fabricated in a lab-scale furnace from 50 kg ingots to the ASTM A508/A508M-16 specification.¹⁷ The forging reduction ratio of the plates was 4.0, and the chemical composition of the produced plates is shown in Table 1. The heat treatment condition is described in Table 2 and consisted of an austenitizing step at 860 °C for 12 h with a subsequent quenching using fan cooling. Tempering was done at 620 °C for 10 h, and the plates were left to cool in the furnace.

A 25×25 mm palladium membrane with a 0.775 mm thickness was used to verify the reproducibility of the hydrogen permeation technique. Palladium was selected because it is an inert material, and its diffusion parameters are widely known.

Metallographic preparation and analysis

Samples for transmission electron microscopy (TEM) were extracted and prepared using a high-resolution focused ion beam (FIB) Tescan LYRA3 GM instrument with a Ga⁺ ion source. The TEM characterization was performed using a Philips CM 200 field emission gun (FEG) operating with a 200 keV electron beam. This instrument, coupled with an energy-dispersive X-ray spectroscopy (EDS) detector, was used to determine the chemical composition qualitatively throughout the sample.

Hydrogen permeation tests

Sample preparation

Circular samples were cut from the as-received material using wire electrical discharge machining (EDM). The samples had a diameter of 35 mm and a thickness of 1.5 mm. Samples were ground to a final thickness using SiC sandpaper with incremental P200, P600, and P1200 grit sizes. Finally, the samples were rinsed with ethanol, dried with nitrogen, and stored in a desiccator. The sample thickness was determined based on the ISO 17081²¹ standard to ensure that the measured parameters reflect the bulk material properties, i.e., that the transport of hydrogen is controlled by volume. As the exposed area had a radius of 8 mm, the thickness was fixed to 1 mm to comply with the 10:1 radius-to-thickness recommendation by the standard.

The need for a coating on the anodic side was stated by Manolatos et al.²² Due to irregularities of electrodeposited coatings in previous tests, samples were sputtered-coated with Pd by magnetron sputtering using a 208HR High Resolution Sputter Coater. SEM and EDS analysis were performed on both the top and cross-sections to verify the Pd layer's thickness and uniformity. Cross sectioning was done by FIB.

Electrochemical hydrogen permeation experiments

Permeation experiments were used to evaluate the hydrogen diffusion parameters of A508 Gr.4N at different charging conditions keeping the rest of the variables fixed (i.e., surface, thickness, and environment). Electrochemical hydrogen permeation studies were conducted as per the Devanathan

and Stachurski experimental approach.²³ The arrangement consisted of two individual semi-cells, i.e., a charging cell and a detection cell, as shown in Figure 1, with the sample clamped in between the two compartments. The evaluation of the results and setup characteristics followed both ISO 17081²¹ and ASTM G148²⁴ standards. The cells' volume was 200 cm³, and the exposed area on both entry and exit sides was 2 cm². Silicon washers covered with high-vacuum grease were used to reduce crevice formation and improve the seal between the samples and the glass cells. The temperature of the electrolyte was controlled using a recirculating bath and maintained at 15 °C.

Silver-silver chloride (SSC) (Ag/AgCl/Cl⁻ in saturated KCl solution) reference electrodes were used with Luggin capillaries to reduce the effect of the solution ohmic resistance in both cells. The Luggin capillaries were filled with 3.5 M KCl. Both charging and detection cells included platinum/iridium 0.25 mm diameter wire and 25×25 mm mesh as counter electrodes.

The solution used in the anodic cell was 0.1M NaOH, in which deaeration was performed by continuous nitrogen purging. The pH measured in the aerated condition was approximately 13. For the charging compartment the solution was 3.5 wt% NaCl, and the measured pH was of 6.5.

A bi-potentiostat with floating grounds was used in both compartments. The anodic side was polarized to +345 mV_{SSC} (+550 mV_{NHE}) to ensure the hydrogen oxidation. Experiments only varied in the applied potentiostatic charging of the entry surface as follows:

- $E_{app,1} = -1.05 V_{SSC}$
- $E_{app,2} = -1.40 V_{SSC}$
- $E_{app,3} = -2.00 V_{SSC}$

The permeation tests started with the stabilization of the anodic side. A deaerated NaOH solution was added from a purging cell to the anodic compartment, in which the anodic surface was polarized to +345mV_{SSC} with no electrolyte in the charging compartment. Nitrogen gas was purged through the cathodic cell to reduce oxide formation while the background current stabilization was performed. The NaCl solution was added to the cathodic compartment once the background current density was lower than 0.1 μA/cm², followed by the corresponding potentiostatic charging. At this point, the nitrogen flow through the cathodic cell was paused.

Once the steady-state was reached, the sample was removed and re-ground using P1200 grit SiC paper. The material loss from this process was negligible. The sample was rinsed and dried with nitrogen and stored in a vacuum desiccator after grinding the cathodic side. Only when evaluating reversible vs. irreversible trapping, the samples were immediately reassembled in the permeation setup after grinding. Three consecutive transients were performed with an applied potential of -1.05 V_{SSC} to investigate the reversible vs. irreversible trapping characteristics of the A508 Gr.4N.

Following the same procedure described above, a palladium membrane was tested to corroborate the reproducibility of the test setup and the accuracy of the obtained parameters. Similarly, three transients were performed with an applied potential of -1.05 V_{SSC}.

Analysis of the results

The flux was calculated using Equation 1 using the hydrogen oxidation current (I_H) from the anodic side.

$$J(t) = \frac{I_H(t)}{Area F} = \frac{i_H(t)}{F} \quad (1)$$

Where F is the Faraday constant (96,485 C/mol), I_H the hydrogen oxidation current expressed in A, and exposed area in cm² units.

At steady-state, the hydrogen sub-surface concentration at lattice sites and reversible traps (C_{OR}) is proportional to the steady-state hydrogen permeation flux J_{ss} .²⁴ When irreversible trapping is

negligible, C_{OR} reflects the severity of the environment, and it can be obtained from Fick's second law as follows:

$$J_{ss} = \frac{D_{eff} C_{OR}}{L} \quad (2)$$

Where D_{eff} is the effective diffusion coefficient, and L is the sample thickness. The D_{eff} values were determined from the permeation transients following ASTM G148²⁴ and ISO 17081.²¹ From the three methods presented in the standards, two of those were implemented in this work to assess D_{eff} . The t_{lag} method is based on the time to reach 63% of the flux at steady-state ($J(t)/J_{ss}=0.63$). D_{eff} is, thus, defined as:

$$D_{eff} = \frac{L^2}{6t_{lag}} \quad (3)$$

The t_b method is based on the breakthrough time, i.e., the time that it takes to detect hydrogen on the anodic side. In this case, D_{eff} is defined as:

$$D_{eff} = \frac{L^2}{15.3t_b} \quad (4)$$

RESULTS

Microstructure

TEM micrographs and EDS element composition maps of A508 Gr.4N are shown in Figure 2(A-F). As reported in a previous work¹⁹ using light optical microscopy (LOM) and SEM analysis, A508 Gr.4N was composed of a complex mixture of lower bainite and tempered martensite. A variety of suspected carbides can be observed in Figure 2(A). Round-shaped particles presented smaller sizes (10-50 nm), whereas anisotropic elongated precipitates showed sizes up to 450 nm. When coupling the TEM analysis with EDS (Figure 2 (B-F)), it can be seen that both the shape and size were correlated to the chemical composition of the suspected carbides. EDS maps (Figure 2(B, C, and D)) revealed that Cr-Mn-C particles had an elongated-type shape and the largest sizes (50-450 nm). For the case of Mo-rich particles, as illustrated in Figure 2(E), suspected carbides also presented an anisotropic elongated shape but had a smaller size (50-100 nm). As seen in Figure 2(F), V-rich particles were found in a discrete round-shape form with sizes that ranged between 5 and 30 nm. Regardless of the chemical composition, particles were predominantly located along lath boundaries.

Hydrogen permeation tests

Reproducibility of the curves—palladium membrane tests

Figure 3 compares three permeation transients obtained using a Pd membrane in which the curves overlapped, indicating adequate reproducibility. D_{eff} values calculated by the t_b method ranged between 4.05 to $4.96 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, whereas for the t_{lag} method, the D_{eff} had a minimum and maximum value of 2.72 and $2.98 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. D_{eff} values calculated using the t_b and t_{lag} methods are displayed as well as the results obtained by Devanathan-Starchuski²³ in Figure 4.

Palladium sputter characterization

The EDS analysis of the top surface confirmed the full coverage of the Pd-sputtered layer on the sample surface. Figure 5 (A and B) depicts areas where FIB removed the sputtered layer, making the contrast in Pd composition evident. The thickness of the coating measured at the cross-section shown in Figure 5(C) ranged from 84 to 105 nm.