

Intergranular Precipitation on the Precipitation-Hardened Nickel Alloy UNS N07725: Double-loop Electrochemical Potentiokinetic Reactivation Test

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ABSTRACT

Precipitation hardened (PH) nickel alloy UNS N07725 used in oil and gas subsea service have experienced several brittle fractures linked to hydrogen embrittlement (HE). The alloy's susceptibility to cracking was associated with the precipitation of a Cr- and Mo-rich phase at grain boundaries (GBs). Since the failed components were compliant with the current standards, developing a new quality control test capable of distinguish susceptible microstructures became a priority for the oil and gas industry. Herein, the double-loop electrochemical potentiokinetic reactivation (DL-EPR) test was optimized for UNS N07725 as an alternative approach to detect microstructures with abundant intergranular precipitation. These precipitates lead to a Cr- and Mo-depletion along the decorated GBs (i.e., sensitization). Thus, the study of the intergranular corrosion susceptibility by the DL-EPR test served as an indirect quantification method of the degree of GB precipitation. The DL-EPR test solution, temperature, deaeration, scan rate, and surface finish were evaluated to distinguish between UNS N07725 batches with different degrees of sensitization. The optimized DL-EPR test conditions were 2 M HCl + 1 M H₂SO₄ + 0.0001 M KSCN aqueous solution at 30°C with a 1.667 mV/s scan rate and a vertex potential of $E_{\text{corr}} + 700$ mV. Results were reproducible and consistent with the metallographically measured degree of GB decoration.

Key words: Alloy 725, Precipitation hardened (PH), DL-EPR, grain boundary, sensitization, hydrogen embrittlement, oil and gas.

INTRODUCTION

UNS N07725 (Table 1) is a Ni-Cr alloy used in numerous oil and gas applications due to its high strength, corrosion resistance, and toughness.¹ UNS N07725's fcc matrix is strengthened by the precipitation of coherent γ' (Ni_3Ti) and γ'' ($\text{Ni}_3(\text{Nb},\text{Ti})$) phases.²⁻⁴ Apart from the strengthening phases, other major microstructural features are the grain structure, and the amount, distribution, and nature of carbides and intermetallic phases.³ The API 6ACRA standard specifies the manufacturing processes and quality control requirements for PH nickel alloys, including UNS N07725, for oil and gas service.² Mannan and Veltry studied the physical metallurgy and phase transformation kinetics of UNS N07725.⁵

The corrosion resistance of UNS N07725 is the result of the high Cr and Mo concentration in solid solution. Cr provides the alloy with excellent corrosion resistance in oxidizing environments by forming a stable passive layer.⁶⁻⁸ Likewise, Mo protects the alloy in reducing environments (such as electrolytes containing HCl, H_2SO_4 , and H_3PO_4) and promotes repassivation during localized corrosion.⁶⁻⁹ Unfortunately, the literature on the corrosion performance of UNS N07725 is somewhat limited.^{3, 10-12} Nonetheless, since UNS N07725 and UNS N06625 (Table 1) have a comparable Cr and Mo content, their corrosion resistances are considered similar.³ Additionally, Nb and Ti stabilize the alloy, reducing the sensitization produced by the intergranular precipitation of Cr-carbides.^{3, 13}

Despite the superior properties of UNS N07725 and other PH nickel alloys, there have been reported brittle failures in relatively benign environments, all associated with hydrogen embrittlement (HE).¹⁴⁻¹⁶ In case of UNS N07725 and N07716, the affected components met the API 6ACRA quality requirements, casting doubt on the current understanding of the HE susceptibility of these PH nickel alloys.^{16, 17} Although the PH nickel alloys failures have led to several investigations to determine the HE resistance of different PH nickel alloys, today there is no clear understanding of the root cause, the HE mechanisms, and most importantly, how to prevent future incidents.¹⁸

Recently, Iannuzzi et al.¹⁶ linked the HE subsea failure of a UNS N07725 batch to a full GB decoration of a nanoscale Cr- and Mo-rich phase. However, the nature of the precipitates and the phase transformation kinetics in the failed components could not be explained at the time. Interestingly, the GB decoration was partially present in all alternative commercial batches studied in their work. The intergranular precipitates could only be observed by Scanning Electron Microscopy (SEM) after a special metallographic procedure not specified in the API 6ACRA standard. Recently, further research on the failed component identified the intergranular phases as M_{23}C_6 carbide and F phase, a σ -related topologically close-packed (TCP) phase not previously reported in commercial Ni alloys.¹⁹ F phase was predominant in the failed component but negligible in an alternative commercial batch of UNS N07725. The oil and gas industry would benefit from a simple test that unambiguously identifies GB decorated microstructures that might be prone to HE.

Towards the development of a quality control corrosion test

Assuming that the GB decoration occurs by a diffusion-assisted transformation, GB precipitation would lead to a depletion of Cr and Mo adjacent to the affected GBs, locally reducing corrosion resistance and promoting intergranular corrosion.⁵ In stainless steel, this difference in Cr and Mo content is commonly referred to as sensitization, and it is the main cause of intergranular attack (IGA). Today, the degree of sensitization (DOS) in nickel alloys is frequently determined by a weight loss test according to the ASTM G28 standard.²⁰ This destructive test requires long

immersion times for highly corrosion-resistant alloys, and it cannot discriminate between small differences in sensitization.²¹

The double-loop electrochemical potentiokinetic reactivation (DL-EPR) technique could be an alternative approach to determine the DOS in nickel alloys. The DL-EPR method is broadly used to identify sensitized stainless steels, but it has yet to be standardized for Ni-based alloys.²² Figure 1 illustrates the cyclic polarization during a DL-EPR test of a sensitized stainless steel. Starting from the open circuit potential (E_{corr}), the material is dynamically polarized to anodic potentials from the active zone to the passive zone, where a stable passivation layer is formed in the regions with enough Cr and Mo. At the vertex potential (E_V), the scan direction is reversed until the original E_{corr} is reached.

During the anodic scan, the activation peak (I_a) is mainly attributed to general corrosion. Therefore, I_a should not depend on the degree of sensitization.^{23, 24} Likewise, in the reverse scan, only the areas with no or an unstable passive layer—e.g., the sensitized regions—corrode and contribute to the reactivation peak (I_r). The DOS is commonly defined as the ratio between the reactivation and activation peaks:

$$DOS (\%) = \frac{I_r}{I_a} \times 100 \quad (1)$$

The main variables of the DL-EPR test are the composition of the electrolyte, temperature, scan rate, and E_V . The standardized test electrolyte for stainless steels is a 0.5 M H_2SO_4 + 0.01 M KSCN aqueous solution.^{22, 23} When immersed in the electrolyte, the stainless steel sample is in the active zone due to the H_2SO_4 content. KSCN acts as an activator, promoting the redissolution of the unstable passive layer in the depleted zone during the reverse scan.²³

Table 2 summarizes DL-EPR test optimizations for relevant Ni-Cr and Ni-Cr-Mo alloys as reported by various authors. A chief difficulty in identifying a suitable DL-EPR electrolyte for highly corrosion resistant alloys is that the Cr and Mo content in depleted areas is often high enough to prevent localized attack.^{24, 25} Most importantly, although the electrolyte used for stainless steels has been successfully optimized for nickel alloys with high a Cr content such as UNS N06690 (Table 2),^{25, 26} it is not an aggressive media for alloys with Mo additions.^{22, 24, 27} Several studies investigated UNS N06625 sensitization using the DL-EPR method by adding between 1.2 M and 2.8 M of HCl to a H_2SO_4 -KSCN solution.^{21, 28-31} Because authors usually present DL-EPR potential vs. current density curves or the final micrographs, but not both, the interpretation of the results might be misleading. In general, DL-EPR tests presented both activation and reactivation peaks and the associated DOSs were consistent with the samples' thermal treatment. However, according to the reported I_r/I_a ratios, the test might not be reproducible enough to serve as a quality control technique.²⁹ Furthermore, Mishra developed a promising DL-EPR test for UNS N10276 (Table 1) in 20 wt.% HCl solution at room temperature.²⁴ The results presented by Mishra clearly showed the effect of the thermal treatment on sensitization.²⁴ Similarly, a 3 M HCl aqueous solution has also been effectively applied to quantify sensitization in (super) duplex stainless steels.^{22, 32}

The objective of the present work was to adapt the DL-EPR technique to identify fully sensitized UNS N07725 microstructures. For that purpose, a DL-EPR test electrolyte was optimized to differentiate between commercial UNS N07725 batches with different degrees of sensitization.

EXPERIMENTAL

Materials

Three types of UNS N07725 samples were studied: (i) a commercial batch that presented the highest degree of grain boundary decoration and was deemed susceptible to HE (affected batch); (ii) a different age-hardened commercial batch that presented a lower degree of sensitization (comparison batch); and (iii) a fully solution treated and not age-hardened batch with clean GBs (annealed batch). The annealed batch was prepared from an as-forged bar heat-treated at 1060 °C for 1 h in a muffle furnace followed by water quenching. The heat treatment was selected to obtain grain boundaries free of intergranular precipitates without significant grain growth.

Table 3 summarizes the chemical composition of the three UNS N07725 batches. The samples metallographic quantification of the intergranular precipitates and the study of the depletion zone were developed elsewhere.³³ Moreover, the nature and relative abundance of the intergranular precipitates in the affected and comparison batches was the focus of a separate publication.¹⁹

DL-EPR test optimization

The optimization of the DL-EPR test electrolyte included the following steps: 1) selection of electrolyte composition; optimization of the 2) acid mixtures and 3) activator content; 4) study of deaeration, scan rate, and surface finish; and 5) DL-EPR reproducibility study. For the selection of the test conditions (steps 1-4), tests were performed in the affected and comparison batches. Likewise, the reproducibility analysis (step 5) included the annealed batch.

Samples of the three batches were prepared for DL-EPR testing. A copper wire was soldered to establish the electrical connection of the working electrode. Specimens were, then, mounted in cold-curing epoxy to cover the electrical contact, leaving an exposed sample area of 0.3 to 1.5 cm². Due to the large number of tests carried out and the limited quantity of the affected batch, samples were reused. Before each test, samples were ground starting with a 120 grit SiC abrasive paper to remove previous corrosion and then polished down to the required surface finish. The absence of previous corrosion was confirmed by LOM before finishing the last polishing step.

DL-EPR tests were performed in a standard three-electrode glass cell. A graphite rod served as the counter electrode, and an Ag/AgCl/3 M KCl electrode was used as the reference electrode ($E_{\text{Ag/AgCl}}=0.210 E_{\text{SHE}}$). 1L of the test solution was prepared shortly before each test. The KSCN was added from a 1 M solution for a precise control of the composition.²⁵ The electrolyte temperature was adjusted with a hot plate and maintained in a water bath during the test. Immediately after the final polishing step, samples were immersed in the test solution. For deaerated condition, N₂ was bubbled through for 1 h to deaerate the solution while the E_{corr} was recorded. The general DL-EPR test procedure consisted of polarizing the specimens from the E_{corr} to $E_{\text{corr}} + 700 \text{ mV}$ and backward to the initial E_{corr} at a given scan rate. After each test, the corrosion mode was determined by LOM. SEM was used in case of unclear pitting, intergranular attack, or both. Table 4 summarizes the scan rate, temperature, sample surface finish and deaeration or aeration conditions used for steps 1-5.

The following criteria were used to determine the best performing test conditions:²⁵

- Curve appearance: I_a shall be independent of the sample's sensitization, and I_r shall appear at the same range of potential than I_a .

- Corrosion selectivity: The I_r peak shall be attributed to intergranular corrosion, minimizing other corrosion modes such as pitting.
- Distinction capacity: The ratio between the DOS of the affected and the comparison batch should be maximized (DOS_{AB}/DOS_{CB}).

RESULTS AND DISCUSSION

Steps 1 to 5 for the optimization of the DL-EPR test solution are presented below. The test solutions for the steps 1 to 3 and the resulting DOS for the affected batch (AB) and comparison batch (CB) are listed in Table 5. The remaining test conditions and the step 4 resulted DOS for both batches are presented in Table 4.

Step 1: Selection of general DL-EPR electrolyte

The electrolytes considered in step 1 were selected based on a literature review and previous experience (Table 5). Solution 1 was a variation of the electrolyte used by Ban et al. for UNS N06625,³⁰ with an [KSCN] of 0.001 M instead of 0.01 M, given that the original composition produced pitting as the primary corrosion mode in UNS N07725 (not shown). For the solution 2, a HCl aqueous solution was evaluated since it has been successfully applied in alternative corrosion-resistant alloys with a lower and higher Mo content. Here, the selected electrolyte concentration was 4.5 M HCl as the 3 M recommended for super duplex stainless steels produced only uniform corrosion in the comparison batch and the 20 wt.% HCl used for UNS N10276 was too aggressive for UNS N07725 (Table 2).^{22, 24} Finally, the electrolyte used for metallographic etching was included as solution 3 since it promoted intergranular attack in the affected batch after long immersion times.³³

Figure 2 compares DL-EPR test curves and presents the corresponding post-test micrographs of the affected batch. The samples did not exhibit a reactivation peak in solution 3 (Figure 2.c), thus the etching solution was deemed not suitable for a DL EPR test. When tested in the HCl H₂SO₄ KSCN electrolyte (solution 1) and the 4.5 M HCl solution (solution 2), both batches presented a reactivation peaks. Additionally, solution 1 produced significant pitting in the two batches. Nonetheless, as the DOS_{AB}/DOS_{CB} was higher and the curve appearance was better with solution 1 compared to solution 2 (Table 5 and Figure 2), solution 1 was selected as the best candidate for the DL-EPR electrolyte.

Step 2: Optimization of the acid content

The affected and comparison batches were tested in several combinations of H₂SO₄ and HCl with a constant content of KSCN (Table 5) to optimize the solution selected in step 1. The KSCN concentration was lowered to 10⁻⁴ M to avoid the pitting corrosion observed when samples were tested in solutions 1 and 4. DL-EPR test curves and selected micrographs are presented in Figure 3 and Figure 4, respectively. All tests met the “Curve appearance” criteria expect from the tests performed in solutions 6, which presented no reactivation peaks (Figure 3.c). Regarding the corrosion modes, most solutions (i.e., 4, 5, 6, 8 and 9) produced intergranular attack in the two samples and negligible intergranular corrosion (Figure 4.a-b and .d-e). In contrast, samples suffered significant pitting in solution 7 (Figure 4.c and .f), comparable to what was observed with the higher concentration of KSCN and the lower H₂SO₄ content in solution 1. Solution 8 (i.e., 2 M HCl, 1 M H₂SO₄ and 10⁻⁴ M KSCN) was selected as the best candidate as it met the “Curve appearance” and “Corrosion selectivity” criteria and resulted in the higher DOS_{AB}/DOS_{CB} .