COMPARATIVE PERFORMANCE OF THREE HIGH-STRENGTH Ni-Cr-Mo ALLOYS IN OILFIELD SIMULATED H₂S ENVIRONMENT

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Abstract

Three Ni-Cr-Mo alloys with 140ksi minimum yield strength, namely 625Plus, 718, and 945X were tested in selected sour environments to evaluate and rank their environmentally-assisted cracking susceptibility. The testing revealed that none of the alloys, stressed to 90% of their actual yield point, cracked as a result of an aggressive 30-day NACE level VII-modified environment (401 ± 9 °F, 500 psia H₂S, 500 psia CO₂ and 151,700 mg/liter chlorides). In a complementary attempt to rank the alloy cracking susceptibility, quasi-static strain rate (SSR) tests per NACE TM0198-2004 were conducted in a modified H₂S-saturated NACE TM0177 Solution A. Following a critical analysis of parameters such as time-to-failure (TTF), percentage reduction in ductility (%ε), percentage reduction of cross-sectional area (% RA) and fractomicrographs, 625Plus was confirmed to outperform its counterparts while some evidence of hydrogen embrittlement was found on 945X.

Introduction

As deeper and higher-pressure hydrocarbon reservoirs are being drilled, explored, and completed with permanent equipment, Ni-Cr-Mo corrosion-resistant alloys (CRAs) with high-strength (i.e., >125ksi) are gaining ground, including for sour service (i.e., environments involving hydrogen sulfide, H₂S). Comparatively, for these corrosive environments, low-alloy steels are limited in both weight-loss and strength due to their sulfide-stress cracking susceptibility when heat-treated for high strength. Despite being normally resistant to weight-loss corrosion, stainless steels like the higher-strength precipitation-hardenable martensitic stainless steels (e.g., 17-4PH, 15-5PH) are all greatly susceptible to sulfide-stress cracking at low temperature and chloride stress-corrosion cracking at elevated temperature. Like low-alloy steels, stainless steels are most often unsuitable for applications requiring long-lasting deployment in high H₂S wellbore environment.

For such sour environments, a restricted number of Ni-Cr-Mo alloys are fit-for-service and available in the market, particularly among the heat-treatable grades that are extensively used among downhole equipment manufacturers. These Ni-Cr-Mo alloys includes 718 (per API6A-718), 725, 625Plus and 945X, an alloy recently introduced as an alternative to 718 and 725 [1]. Owing to both their excellent corrosion resistance and heat-treatability, all these alloys may be reliably produced to yield strengths in the vicinity of 140 ksi while still exhibiting proper

microstructures, elevated toughness, and high cracking resistance in oilfield fluids. Of these alloys, 625Plus at 140ksi minimal yield strength is widely seen as being the ultimate precipitation-hardened Ni-Cr-Mo alloy, partly due to its high nickel and molybdenum contents. In contrast, 718 and 945X have somewhat similar compositions, making it unclear if one alloy distinctively surpasses the other. In this paper, two objectives are pursued:

(1) Determine whether 140ksi alloys such as 625Plus, 718, and 945X can resist cracking under static tensile loading conditions, selected to be beyond the industry-accepted limits for H₂S exposure, specified in NACE MR0175

(2) Determine if one of those alloys truly stands apart, and in the process, perhaps rank all three alloys in terms of their resistance to environmentally-assisted cracking.

Experimental Procedure

For this study, fully heat-treated Ni-Cr-Mo alloys such as 625Plus (N07716), 718 (N07718) 945X (N09945) were selected from mill certificates with requirements that their yield strengths are all in excess of 140ksi, but below the maximum hardness values recommended by NACE MR0175 / ISO15156. The 718 sample complied with API specification 6A718. The chemical compositions of all as-received alloys are disclosed in Table 1 for reference and comparisons. It is noteworthy that 718 and 945X are nearly indistinguishable in their compositions with the exceptions of titanium, columbium (niobium), and cobalt. This feature alone, along with similar mechanical properties (reported in next section), is important to remember when reading the remainder of this paper.

Table 1: Chemical compositions (wt.%) of 718, 625Plus and 945X

Wt.%	C	Mn	P	S	Si	Ni	Cr	Mo	Al	Ti	Cb + Ta	Cu	Co	Fe
718	0.019	0.11	0.008	0.0002	0.1	54.6	18.5	3.02	0.46	0.9	5.12	0.04	0.03	82.9
625Plus	0.016	0.09	0.009	0.0002	0.12	61.2	20.9	8.05	0.22	1.4	3.33	0.06	-	95.4
945X	0.014	0.07	0.01	0.0007	0.5	53.6	18.7	2.87	0.51	1.01	4.96	0.05	0.19	82.4

In order to provide the most representative samples, tensile and C-rings specimens were machined from mid-radius locations of 6 to 8in bar stock, with stressing direction longitudinal. Environmentally-assisted cracking was evaluated using two well-known test methods: NACE TM0177 Method C (stressed C-ring tests) and NACE TM0198 (slow strain-rate, also referred as SSR). Typical dimensions for the NACE TM0177 C-ring test are shown in Figure 1. In this first test, the C-rings are tensile stressed to a predetermined value (herein 90% of actual yield strength at temperature) and exposed in a pressurized autoclave to a specified sour environment (Figure 2). Other test parameters such as aqueous phase volume, pH buffering, fixtures, gas preloading, autoclave characteristics, and test solutions are addressed in Sections 2 to 7 of NACE TM0177. To consistently evaluate cracking susceptibility, all C-rings were exposed to the same environment: 401 ± 9°F, 500 psia H₂S, 500 psia CO₂ and 151,700 mg/liter chlorides, fully de-aerated (<10ppb O₂). Note that this test environment is more aggressive than the so-called NACE level VII environment. Upon completing the tests (after 30 days), each C-ring was carefully inspected for cracks using both dye-penetrant and 50X visual examination of metallographic cross-sections.

Figure 1: Schematic representation of a NACE TM0177 C-ring for assessing environmentally-assisted cracking susceptibility.

Figure 2: Schematic illustration depicting a stack of C-rings positioned within an autoclave in the aqueous phase of a sour test solution.

In an attempt to rank alloy environmentally-assisted cracking susceptibility, the static C-ring tests were complemented by slow-strain rate (SSR) tests. In this test, the specimens (thus alloys) are strained to fracture and compared using ratios of time-to-failure (TTF), percentage reduction of area (% RA) and percentage elongation (% ϵ) measured in the sour test environment relative to that in air. Following the SSR tests, the specimen fracture surfaces were examined using scanning electron microscopy to gain further insight on the cracking mechanisms. Note that a special attention was given to secondary cracks in the gauge length and away from the primary fracture.

Results & Discussion

In Figure 3 are summarized the mechanical properties of all three tested alloys at both ambient and test temperature. Values of the yield strength at temperatures were recorded and used to properly stress the C-rings. Figure 4 shows a washed C-ring after being subject to the 30-day autoclave tests with the sour test environment. The testing revealed that none of the C-rings, from either 625Plus, 718, or 945X, exhibited any cracking, thereby indicating all selected alloys can survive the selected test environment for 30-days, and potentially much longer. However, some minor pitting corrosion, potentially precursor to cracking, was observed on many of the exposed test specimens.

Figure 3: Mechanical properties of the tested alloys at ambient and at test temperatures.

Figure 4: Photographs of a tested C-ring with accompanying rectangular corrosion coupon.

In Figure 5 are photographs of the SSR specimens after tests in air and the sour environment. Note that all tensile specimens exhibit a distinct necking, clearly indicating that all three alloys retained significant ductility despite the corrosive condition. Furthermore, visual examination of these specimens confirmed the absence of secondary cracking. For the specimens exposed to the sour environment, it may be noted that a dark scale indicative of sulfide corrosion residues was also encountered. This dark scale may be seen in the threaded (unwashed) part of the test specimens.

Figure 4: Photographs of the SSR specimens tested in air and in the sour environment. All three alloys revealed distinct necking, pitting, and indication of a sulfide film.

Figure 5 summarizes the slow-strain test (SSR) results. First note that the reported values are all lower than that in air, as expected from the corrosive environments, and also quite comparable, therefore suggesting that all three alloys exhibited relatively similar cracking resistance. Of all properties, time-to-failure (TTF) may be analyzed first. In increasing order of longevity are 718, 945X and 625Plus. As anticipated, the greater TTF and elongation ratios of 625Plus indicate that this alloy outperforms both 718 and 945X, although the reduction of area is more severely impacted. However, overall, the test results show no significant difference between any of the alloys. The results for 718 and 945X are almost indistinguishable, as might have been expected from their comparable chemical compositions (Table 1).

Figure 5:
Degradation ratios of mechanical properties of 625Plus, 718 & 945X in the selected sour environment

Figures 6a-c depict scanning-electron micrographs of fracture surfaces seen on 625Plus, 718 and 945X test specimens strained to failure in the selected sour environment. First note that dimples, indicative of micro-void formation and coalescence (thus ductile behavior) may be seen in 625Plus as opposed to a more mixed quasi-cleavage and dimpled fracture mode in both 718 and 945X. When specifically comparing 718 and 945X, 945X also appeared to exhibit more facets (partially brittle behavior), thereby somewhat correlating with the reduced ratio of % RA reported in Figure 5.

Figure 6: SEM fracture surfaces of the SSR specimens:

- (a) micro void coalescence on 625Plus, indicative of a ductile failure,
- (b) a mixed quasi-cleavage and dimpled fracture on 718,
- (c) more cleavage on 945X.

Figure 7 shows voids nucleated at small second-phase particles (presumably strengthening precipitates) on 625Plus. It is commonly accepted that voids are nucleated at dislocation cell boundaries, or slip-band intersections ahead of cracks, and serve to re-sharpen cracks so that crack-tip-opening angles are smaller than the angle between the two slip planes. Figure 5(b) shows microscopically dimpled fracture surfaces on 718. Also seen are crack fronts parallel to the line of intersection of crack planes with slip planes.

Figure 9 discloses several scanning-electron micrographs of the fracture surface seen on 945X. Sharply different topological features may be seen on this alloy. These features, precisely striations, are common on fatigue-tested specimens, but rarely reported in quasi-statically tested alloy specimens. Here, and based on other studies [5], these striations are believed to point out localized slip lines, possibly deformation twins, that had been induced by hydrogen-charging conditions. In full context, the pictures of Figure 6 also suggest that 945X (at least the tested alloy) may be slightly more susceptible to environmentally-assisted cracking, specifically hydrogen embrittlement. Though more detailed studies are required, some explanations may be now postulated for the seemingly reduced ductility observed in 945X in the selected sour environment.

Figure 7: Voids at small second-phase particles (likely strengthening precipitates).

Figure 8: Microscopic dimples along a possible low-index crystallographic planes bisecting two active slip planes.

Figure 9: (a-c) Some evidence of slip (possibly twinning) along the gauge length of a 945X SSR specimen.

Fundamentally, environmentally-assisted cracking (including hydrogen embrittlement, H_2E) depends upon chemical composition, microstructure and tensile stress level. Among microstructural features, important factors include irreversible and reversible traps, stacking faults (including dislocations, twins), precipitates and inclusions [2]. A popular explanation is that, H_2E develops when atomic hydrogen diffuses to internal structural defects (referred as collectors) and is recombined to its molecular state to create microcracks [3]. In the case of reversible embrittlement, ductility may be recovered due to hydrogen desorption, an event that is more favorable at elevated temperatures. In the case of irreversible embrittlement, associated with the formation of microcracks and other defects), time and temperature do not restore affected alloys to their ductile states. In all three alloys, there is evidence that hydrogen found its way in via various diffusion routes involving reversible and irreversible traps. Recall that all three Ni-Cr-Mo alloys were covered by a scale, identified to be a sulfide-rich scale because of the presence of H_2S in the autoclave. This likely-to-be sulfide scale is known to be a hydrogen recombination poison, meaning it does promote diffusion of atomic hydrogen. Once hydrogen has found its way from the corroded surface to the bulk alloy, the rate of penetration of hydrogen is a function of diffusivity and solubility, two properties that likely differ in all three alloys. However, recall that atomic diffusion occurs largely along interfaces but also through the lattice via vacancy mechanisms. As explained by the “Corrosion Enhanced Plasticity (CEP) Model” [6], vacancies are generated by localized anodic dissolution and hydrogen evolution by cathodic reaction at depassivated crack tips. There, activated dislocations along slip bands form pile-ups

interacting with obstacles such as other defects, including precipitates, and initiate cracking. To summarize, this study confirms that chemical composition is not the only important factor controlling environmentally-assisted cracking. When 718 and 945X are for instance compared (two nearly indistinguishable alloys by their chemistry), differences between trap sites and diffusion paths should also be considered to explain the seemingly slightly more brittle behavior observed in the 945X alloy selected for this study.

Conclusions

These following may be concluded based on this first study aimed at comparing 625Plus, 718 and 945X, three alloys commonly found in oilfield downhole equipment:

- 625Plus outperforms both 718 and 945X in environmentally-assisted cracking resistance.
- 718 and 945X have equivalent performance in the selected sour environment.
- Cracking by microvoid coalescence (ductile behavior) is present on all three alloys, particularly on 625Plus. Microvoid nucleation and coalescence was also seen to occur predominantly from particles (presumably strengthening precipitates).
- Mixed quasi-cleavage and dimples were seen on 718 and 945X, with increasing cleavage on 945X (in partial agreement with the reduced percentage %RA for the two alloys compared to that of 625Plus).
- Various microstructural observations infer that an adsorption-induced localized slip process is at least in part responsible for environmentally-assisted cracking, particularly on 945X.

Finally the hydrogen embrittlement of 625Plus, 718 and 945X (pointed out by this study) is to be further assessed and discussed in upcoming publications.

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