

On the Corrosion of Commercial Coatings, Surface Treatments, and Carbides for Servicing Equipment Operating in Highly Sour Production Environments

Manuel Marya
Schlumberger Technology Corporation
200 Gillingham Lane
Sugarland, Texas 77478, USA

ABSTRACT

The corrosion resistance of various coatings, surface treatments (from different nitriding processes), and sintered carbides (among traditional and new commercial grades) has been evaluated in highly sour environments and benchmarked against corrosion-resistant alloys. The laboratory testing consisted of series of 4,000 psi (20.6 MPa) autoclave tests with 1500 psi (10.3 MPa) hydrogen sulfide (H₂S), temperatures up to 375°F (191°C), and exposures of 15 and 30 days. Corrosion was described both qualitatively (e.g., discoloration, pitting, spalling, corrosion byproducts) and quantitatively (i.e., with average weight-loss corrosion rates). For sintered carbides, crevice corrosion was also investigated to replicate the corrosion over stagnant sealing surfaces. Overall, this investigation establishes that (1) nitriding surface treatments are highly unequal and do not corrode more than well-established coatings currently in use, (2) certain coatings can be highly protective, especially when applied onto alloy substrates that are H₂S weight-loss corrosion resistant, (3) carbide grades are less susceptible to weight-loss corrosion despite major variations in performance. Through series of complementary tests, this investigation also concludes that some of the current materials technologies appear to remain fit-for-service for highly sour environments.

Key words: corrosion, nitriding, plating, spalling, tungsten carbide, hydrogen sulfide

INTRODUCTION

Coatings, surface treatments, and carbides all represent separate families of advanced materials that, despite being sometimes overlooked compared to structural alloys, are critical to the proper and long-lasting functioning of downhole exploration or production equipment.¹⁻⁴ Corrosion-resistant alloys (CRAs) such as Alloy 17-4PH (UNS S17400) and Alloy 718 (UNS N07718) are high-strength precipitation-hardened alloys found in oilfield equipment at surface, subsea, and downhole.⁵ For material evaluation purposes, Alloy 17-4PH and Alloy 718 well represent the broader spectrum of CRAs in use across oilfield applications. Alloy 17-4PH is a stainless steel that is often utilized in the HH1150 NACE MR0175/ISO15156⁶ condition at 105 ksi (723 MPa) minimum yield strength and 33HRC maximum hardness. Alloy 718 is a nickel-based alloy for applications requiring greater strength and environmental

⁽⁶⁾ National Association of Corrosion Engineers (NACE), 15835 Park Ten Pl, Houston.

⁽⁶⁾ International Standard Organization (ISO), 8 Chemin de Blandonnet, CP 401 – 1214, Vernier, Geneva, Switzerland.

⁽⁷⁾ American Petroleum Institute (API), 1220 L. St., N.W., Washington, DC 20005-4070.

resistance, particularly against sulfide stress-cracking (SSC). Alloy 718 is typically used in the API 6A CRA ⁷ condition, and since recently allowed with a maximum hardness of 45HRC and a corresponding minimum yield strength of 150 ksi (1034 MPa). ⁷ It shall be noted that for servicing equipment, Alloy 718 is also utilized in the aerospace conditions, most commonly as per AMS 5663. ⁸ Regardless of their metallurgical conditions, both Alloys 17-4PH and 718 can lack the necessary hardness and abrasion resistance required by either dynamic sealing or high erosion applications. Surface treatments like liquid-bath nitriding, plasma nitriding, and coatings such as electroplating, electroless plating, or vapor deposition are well-established means to alter the tribological behavior of CRA surfaces. ⁹ Surface treatments and coatings for valves, chokes, and general equipment with reciprocally moving parts are generally thin by design, yet have been field proven in countless abrasive applications. In applications involving high flow velocities, particularly in the presence of solid particles, surface treatments and coatings are limited by their thickness, adhesion strength, and corrosion performance. ⁹ In contrast, the sintered carbides (tungsten carbides) typically possess the hardness demanded by wear service applications, in combination with minimal transverse rupture strength and minimal (Palmquist) toughness. Like surface treatments and coatings, sintered tungsten carbides are available in many proprietary flavors, thus with a range of oilfield performances. Sintered tungsten carbides are considered the materials of choice for erosion service. They are well established in flow control while also utilized for miscellaneous bushings and bearings. ¹⁰

In this manuscript, both nitriding (as produced by various processes) and engineering coatings with a thickness of 2-4 mils (50-100 μm) have been professionally applied to test articles of Alloys 17-4PH and 718 (among others), then subjected to wet, highly sour, and increasingly corrosive autoclave environments. Examinations of these test articles were conducted to better understand and further establish useful performance limits. Likewise, nine commercial tungsten carbides were exposed to the same environments, and compared for their performance to the surface treatments and coatings.

EXPERIMENTAL PROCEDURE

In preparation for autoclave testing, test articles made of Alloys 17-4PH, 718, and sintered tungsten carbides were acquired and complemented by 4130 (UNS G41300) low-alloy steel, Alloy K500 (UNS N05500), and Alloy 625Plus⁺ (UNS N07716). Two main test article geometries were considered, with no expected consequence on the end results due to common surface area normalization. For surface treatments and coatings, rectangular test articles ($1^{1/2} \times 6 \times 1/8$ in, 38.1 x 152.4 x 3.2 mm) were utilized to permit additional analyses beyond the scope of this paper. For tungsten carbides, cylindrical test articles (1-in or 25.4-mm diameter, $1/2$ -in or 12.7-mm thick) were preferred. All test articles were pierced with a $1/4$ -in or 6.4-mm hole to enable their proper handling.

For surface treatments and coatings, the rectangular test articles were dispatched to selected professional applicators across the United States and Europe. Out of pragmatic considerations, all surface treatments consisted of nitriding by the QPQ (Quench-Polish-Quench) process (test articles referred as 718QPQ, 174QPQ) and two proprietary low-temperature ion nitriding processes (test articles referred as 718S, 174S, 174E). The coatings consisted of electroless nickel platings, including: (i) the traditional ASTM B333¹¹ 11-wt.% phosphorus grade with two heat-treat conditions (EN, DEN), (ii) a proprietary PTFE-infiltrated mid-phosphorous electroless plating (NX), and (iii) a boron-enriched nickel plating (NiB). Other coatings were produced by electrolytic processes (718LY, US81, US84) or chemical vapor deposition; the latter included a nanostructured tungsten carbide coating (HD K500, HD 174) and a Diamond-Like Carbon coating (DLC-I) that had been applied on a 4130 low-alloy steel. Test articles of Alloys 718, 17-4PH, and K500 were used as reference for comparisons against test articles processed with surface treatments and coatings. It shall be noted that the Alloy 718-test article, due to a procurement constraint, was selected from an additively manufactured product, well understanding this material behavior is expected to deviate slightly from the normal wrought-stock material. ¹² The cylindrical carbide

test articles were produced from nine commercial grades to establish their corrosion resistance against the bare alloys, surface treatments, and coatings. These articles were produced in a super-finished condition, as in typical tool applications. Details on these carbides are provided in the results and discussion section.

Three autoclave environments were produced, with intent to make the second and third environments more aggressive and with some commonality with the first test to facilitate test article ranking. Table 1 describes these three environments. By intent, Test #2 had twice the durations and twice the chlorides of Test #1, a condition geared at promoting pitting corrosion. Test #3 aimed at further increasing the severity of the test environment through concurrent increases in both chlorides and temperature. Note that the hydrogen sulfide (H₂S) partial pressure was held constant and is considerably in excess to the recommendations of the NACE MR0175/ISO 15156⁶ document for Alloy 718 (for general equipment, Alloy 17-4PH is restricted to 0.5 psi or 3.4 kPa H₂S).

Table 1
Basic description of the environmental test conditions for Tests 1-3

Test	P _{Total}	pp H ₂ S	pp CO ₂	Cl- in ppm	T	pH _{initial}	Days
#1	4,000 psi (27.6 MPa)	1,500 psi (10.3 MPa)	500 psi (3.4 MPa)	30,000	300°F (149°C)	3.10	15
#2				60,000		3.08	30
#3				90,000	375°F (191°C)	3.10	30

All test articles were photographed and weighed pre- and post-environmental testing. Where perceptible changes were recorded, the surfaces were further surveyed by optical microscopy, scanning electron microscopy (SEM), and electron-dispersive spectroscopy (EDS).

RESULTS AND DISCUSSIONS

Surface treatments and coatings are first addressed, followed by the carbide grades. Visual inspection, weight-loss corrosion measurements, SEM and EDS examinations are consecutively described and discussed. Comparisons of coatings, surface treatments, and carbides are completed at last.

Surface Treatments and Coatings

Figure 1 is a mosaic of macrographs for test articles from Test #2 (Table 1), where surface treatments and coatings can be first visually assessed. In general, surface treatments and coatings appear to be greatly unequal in their sour-service performance. Alloy 718 in bare condition only stains slightly and can serve as a common reference from this point forward. Over most of its surface, Alloy 718 remains shiny, exhibiting only isolated pits that are visible to the naked eye. In comparison, a lot more staining occurred on the nitrided test articles, with a significantly darker discoloration on Alloy 17-4PH (174QPQ) than on Alloy 718 (718QPQ). All three nickel-base electroless coatings, including EN, DEN, and UT consistently show a golden discoloration, with evidence of large spalling in areas, particularly nearby edges. The US81 electroplated coating is observed to tarnish slightly, yet with no sign of spalling. The K500 test article with the HD coating, a coating consisting of nanostructured carbide, was surprisingly seen to underperform its peers due to major spalling.⁴ The DLC-I coating also reveals some clear debonding, also near the edges. This last result clearly indicates that this specific DLC-I coating (as had been produced by the selected applicator) is most unsuitable for sour service.

Figure 2 summarizes major results from both Tests #1 and #2 where weight changes for each surface treatment and coating have been converted to average corrosion rates (in mpy). Due to resource limitations, please note that some test articles were only tested once; e.g., in an event of poor corrosion,

some coatings were abandoned after a single test and replaced in later tests. In Figure 2, the y-axis log scale first indicates that corrosion rates vary by about four orders of magnitude, with Alloy 17-4PH positioning itself as the least prone to corrosion, along with the low-temperature nitrided 174E not far behind. Differently, the nickel electroplatings such as 718LY and 174NX showed among the worse corrosion rates. On these last two coatings, most of the electroplated surfaces are seen to spall. Since these coatings are proprietary, details on these coating application and composition remain unknown. However, it may be speculated that these coatings failed due to a combination of the following: (1) improper adhesion to their base substrates, (2) high interfacial stresses between coating and substrate materials, (3) intrinsically poor corrosion resistance due to holidays and impurities, among other plausible reasons. With these coatings now established as unsatisfactory, they were excluded from subsequent tests, with no further analyses completed. However, since the EN coating is well-established in oilfield tools, it was further evaluated despite being associated to extensive corrosion.

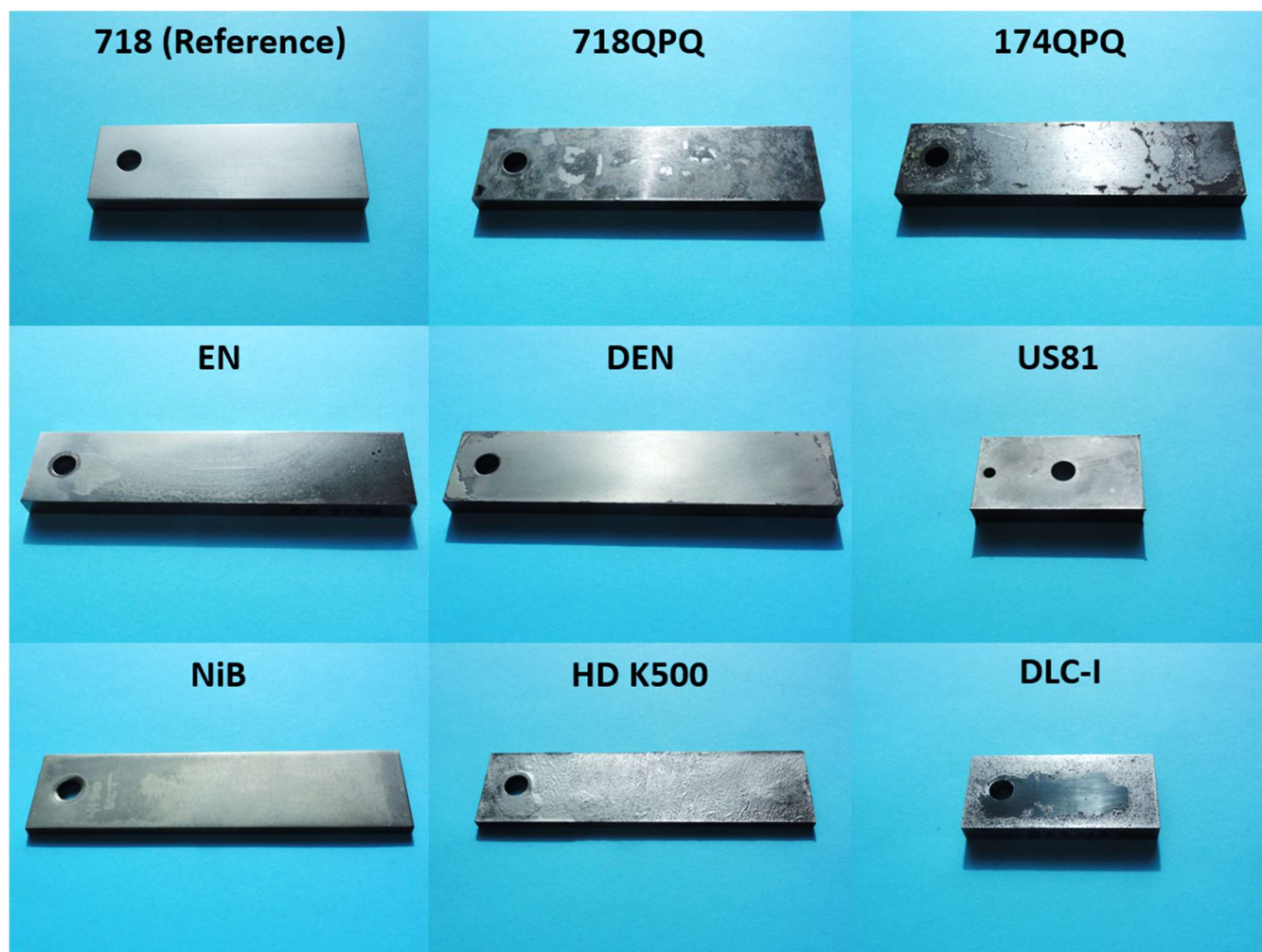


Figure 1: Selected test articles after a 30-day exposure to the environment of Test #2. All pictures were taken after a short ultrasonic cleaning for descaling purposes. Note that Alloy 718 is visually unaffected whereas major disparities in performance exist between surface treatments and coatings.

Before digging deeper into the specific performance of each surface treatment and coating, the corrosion results for Alloys 718, 17-4PH, and K500 are first examined. Among all three alloys in Figure 2, Alloy 17-