Stainless steel with a tantalum surface alloy resists corrosion in an aggressive acid environment

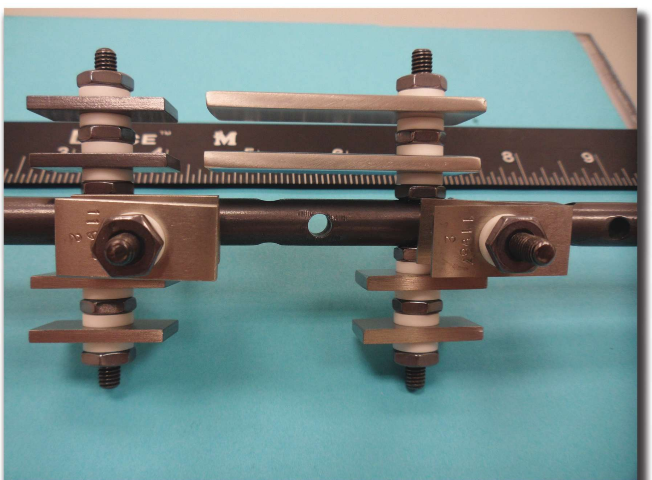
In oil well production, pumping stimulation acids into an oil reservoir through tubular piping, also known as acidizing, is commonly used to clean tubular deposits, remove formation damage, and increase formation porosity. The acidizing environments are aggressive and almost every alloy used in the process experiences high corrosion rates.

To evaluate the corrosion resistance of several corrosion-resistant alloys (CRAs) in these environments, research laboratory Honeywell Corrosion Solutions (Houston, Texas) conducted a study in the laboratory that exposed samples of various CRAs to two simulated deep well acidizing environments. According to NACE International member Brian Chambers, the senior research engineer with Honeywell Corrosion Solutions who conducted the study, corrosion damage is expected to occur in high-temperature acidizing solutions, even with high doses of the proper inhibitors. Because the tubular piping is exposed to the acidizing solutions for short periods of time, the industry generally accepts corrosion rates that are <2,000 mpy (<50.8 mm/y).

Chambers explains that the study was conducted to gain an understanding of how these alloys would perform in the acidizing environments and to determine what the corrosion rates would be if the materials were exposed to stimulation acids for an ultra deep well. Both general and localized corrosion were evaluated. In the study, one test environment represented a mild acidizing condition with 10% acetic acid ($C_2H_4O_2$) and the other test environment corresponded to an aggressive acidizing condition with 10% hydrochloric acid (HCl), 10% $C_2H_4O_2$, and 0.1 MPa hydrogen sulfide (H_2S). Neither solution contained any corrosion inhibitors; corrosion rates in uninhibited acidizing solutions reflect a worst-case scenario and are thought to better represent actual acidizing operations under flow or conditions where inhibitors were already consumed at shallower depths in the well. The alloys tested were Type 316L stainless steel (SS) (UNS S31603), nickel-based C276 (UNS N10276), titanium alloys Ti 6-4 (UNS R56400) and Ti 6-2-4-6 (UNS R56260), and Type 316L SS with a tantalum surface alloy.

Another goal of the study, Chambers adds, was to prove a piece of equipment that could withstand the acidizing environments simulated in the tests. "Our laboratory specializes in extreme environment exposure to test for corrosion and cracking, so most of our equipment is constructed of C276. We had already run into a problem when we attempted tests in these acidizing environments, and caused damage to very expensive pieces of equipment," Chambers explains. When the Honeywell researchers started to experience degradation of their equipment, they approached Tantaline (Waltham, Massachusetts), a producer of tantalum surface alloys, about treating some of their lab equipment with its tantalum surface alloy process to determine if the Ta surface alloy would hold up under the corrosive acidizing environments when conducting tests.

Tantalum is known as one of the most corrosion-resistant materials available, explains Dean Gambale, president of Tantaline. The problem with tantalum, he says, is that it is very expensive, difficult to machine, and difficult to fabricate into



A view of the Ta-surface-alloyed specimen rack before testing in the mild acidizing environment. Photo courtesy of Honeywell Corrosion Solutions.

A view of the specimen rack following exposure to the aggressive acidizing environment. The Type 316L SS coupons on the upper right side of the rack and titanium alloy coupons on the left side of the rack were completely dissolved. Photo courtesy of Honeywell Corrosion Solutions.

parts. Tantaline has developed a proprietary vapor-deposition process where commercially pure tantalum is chemically reacted and vaporized in a furnace heated to a temperature between 700 and 900 °C. The high temperature provides conditions suitable for diffusion and surface bonding of the vaporized Ta to a fabricated metal product at the atomic level. Gambale emphasizes that the resulting surface alloy is not a metallic coating with a distinct interface between the two materials. The interface or alloy zone between the Ta surface alloy and the substrate is a metallurgical bond that gradually blends the Ta with the substrate metal until the surface metal becomes pure Ta. The pure Ta surface alloy is typically 50-μm thick.

All internal parts of the autoclave used in the tests were constructed of alumina ceramic or Ta-surface-alloyed Type 316L SS. The specimen test rack was also made of Type 316L SS with a Ta surface alloy. The test coupons were stamped with unique identification numbers, and the location of each set of coupons on the specimen rack was noted in the event that identification numbers were illegible after being exposed to the acid solutions. The coupon exposure for each acidizing environment was 8 h at 450 °F (232 °C), after which the autoclave was quickly cooled and the coupons were removed and inspected.

TABLE 1

Corrosion Rates in a Mild Acidizing Environment—10% $C_2H_4O_2$

Material	Weight Loss mg	Corrosion Rate mpy (mm/y)	Average Corrosion Rate mpy (mm/y)
Type 316L SS	30.6 45.8	193 (4.9) 291 (7.4)	242 (6.1)
C276	2.1 2.0	12.2 (0.3) 11.6 (0.3)	11.9 (0.3)
Ti 6-4	0.3 0.1	3.3 (0.1) 1.1 (0.0)	2.2 (0.1)
Ti 6-2-4-6	0.0 –0.1	0.0 0.0	0.0
Ta-surface-alloyed Type 316L SS	–0.3 –0.3	0.0 0.0	0.0

TABLE 2

Corrosion Rates in an Aggressive Acidizing Environment—10% HCl, 10% $C_2H_4O_2$, and 0.1 MPa H_2S

Material	Weight Loss mg	Corrosion Rate mpy (mm/y)	Average Corrosion Rate mpy (mm/y)
Type 316L SS	>5,787 (dissolved) >5,747 (dissolved)	>36,506 (>927) >36,517 (>928)	>36,517 (>928)
C276	3,604 3,589	20,901 (531) 20,893 (531)	20,897 (531)
Ti 6-4	>3,733 (dissolved) >3,718 (dissolved)	>41,341 (>1,050) >41,312 (>1,049)	>41,341 (>1,050)
Ti 6-2-4-6	>1,260 (dissolved) >1,259 (dissolved)	>16,289 (>414) >16,231 (>412)	>16,289 (>414)
Ta-surface-alloyed Type 316L SS	–1.7 –1.7	0.0 0.0	0.0

In the test with the mild acidizing condition (10% $C_2H_4O_2$), all the alloys exhibited corrosion rates well below the 2,000 mpy acceptability criteria, Chambers says. The results are shown in Table 1. The corrosion rates in the test with the aggressive acidizing condition (10% HCl, 10% $C_2H_4O_2$, and 0.1 MPa H_2S) were extremely high for all the alloys evaluated except for the Ta-surface-alloyed Type 316L SS, which exhibited no corrosion. The Type 316L SS, Ti 6-4, and Ti 6-2-4-6 coupons were all completely dissolved during the 8 h exposure. Table 2 displays the results for this test.

"We were expecting the Type 316L SS to be completely dissolved and were anticipating extremely high corrosion rates for C276," Chambers comments. "There weren't many studies previously done on the titanium alloys that would tell us what would happen, so the test results were interesting for certain, especially considering that the titanium alloys were being considered for tubulars in ultra deep wells because of their high corrosion resistance in most cases, cracking resistance, and the lightweight nature of the alloy. It was enlightening," he adds.

The results of the study also demonstrated that the laboratory testing equipment treated with the Ta surface alloy process successfully withstood the highly corrosive, high-temperature acidizing environments, which is critical for the lab's equipment integrity.

More information on the Honeywell study can be found in CORROSION 2011 paper no. 11106, "Performance of Tantalum-Surface Alloy on Stainless Steel and Multiple Corrosion Resistant Alloys in Laboratory Evaluation of Deep Well Acidizing Environments," by Brian Chambers, Anand Venkatesh, and Dean Gambale.

Contact Brian Chambers, Honeywell Corrosion Solutions—e-mail: Brian.Chambers@Honeywell.com; and Dean Gambale, Tantaline—e-mail: dgambale@tantaline.com. MP

—K.R. Larsen