Materials Testing for use in Strong H_2S Acidizing Environments

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With the world's growing energy demands and depleting oil reserves, deeper and harder to reach oil reserves are being explored and drilled. With the technology that exists today, oil well depths beyond 35,000 ft are being drilled using technology and know-how developed over decades within the oil and gas industry. The materials needed to survive in the extreme conditions are the limiting factor for successful operation especially in wells containing hydrogen sulfide (H_2S), or sour gas, under acidizing conditions.

Oil well stimulation by acidizing is a common practice involving the use of strong acids pumped through the tubular and into the oil formation. Various acids such as hydrochloric (HCl), hydrofluoric (HF), acetic acid, and formic acid are commonly used, which can cause high corrosion rates on nearly every alloy used in production. Corrosion rates can be greatly accelerated in the presence of H_2S at high temperatures and pressures. Corrosion damage, even with the use of high doses of the proper inhibitors, is expected to occur in acidizing solutions at elevated temperatures.

This article discusses a laboratory study to evaluate the corrosion resistance of multiple alloys under acidizing conditions to help identify which materials are suitable in these extreme conditions. Alloys investigated included stainless steel (316L), nickel-base alloy (C276), titanium alloys (Ti 6-4 and Ti 6-2-4-6), and a tantalum surface alloy (316L surface-alloyed with tantalum). Two tests were conducted using two acidizing environments representing a mild condition (10% acetic acid) and an aggressive condition (10% HCl, 10% acetic acid, 15 psia H_2S); neither solution contained any corrosion inhibitor. Tests were conducted at 450°F (230°C) to represent the bottom-hole temperature of a deep well.

Results of Corrosion Tests with 15% HCl + Inhibitor 1

TEST	1A-1		1A-2		1A-3		1A-4	
CONDITIONS	200 F/CO_2		400 F/CO_2		200 F/H_2S		400 F/H_2S	
STAGE	1	1, 2, 3	1	1, 2, 3	1	1, 2, 3	1	1, 2, 3
4130								
13 Cr	O	O	O		O	O		
22 Cr	O	–	O		O	O		
25 Cr	O	–	O		O	O		
28 Cr	O	O	O	X 2	O	O	O	X 2
42 Ni	O	O	O	X 3	O	O	O	X 3
925	O	O	O	X 3	O	O	O	X 3
718	O	O	O	X 3	O	O	O	X 2
52 Ni	O	O	O	X 3	O	O	O	X 3
ALLCORR	O	O	O	X 3	O	O	O	X 2
C-276	O	O	O	X 3	O	O	O	O

WEIGHT LOSS CORROSION
- EITHER > 2000 MPY OR SPECIMENS DESTROYED BY CORROSION DURING TEST PERIOD.
- < 2000 MPY (5.5 MPD)
- NOT TESTED

STRESS CORROSION CRACKING
- O - NO FAILURE
- X - FAILURE (2, 3 refers to stage of test)

Fig. 1 — *Results of corrosion and cracking evaluations in a variety of conditions with inhibited 15% HCl.*

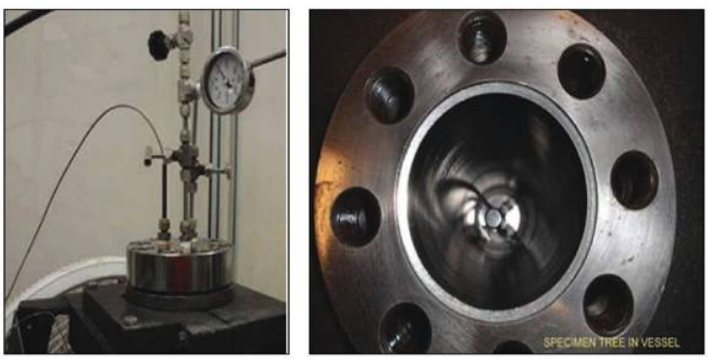

Fig. 2 — *Photographs of Ta surface-treated autoclave.*

Experimental Setup

Due to the highly corrosive nature of the environments, an autoclave constructed of 316L treated with a Ta surface-alloy was used to prevent excessive corrosion and subsequent possible failure of the pressure vessel. All internal parts of the autoclave were constructed of either Ta surface-alloyed 316L or alumina ceramic. Photographs of the autoclave assembly and internals are shown in Fig. 2. As illustrated in this article, the Ta surface-alloy was critical for equipment integrity in conducting the acidizing experiments.

The Ta surface alloy on all equipment, accessories, and corrosion coupons was prepared using a proprietary process developed by Tantaline. The Ta surface alloy process involves the production of a gaseous atmosphere of tantalum that grows the Ta metal onto and into the substrate (Fig. 3) Ta metal forms over the substrate-Ta interface, providing the chemical and corrosion resistance properties of pure Ta. This process occurs at nanoscale dimensions and at high temperatures creating a metallurgically bonded Ta layer superior in durability to traditional coatings or electroplating.

The objective of the study was to evaluate corrosion in the worst-case condition (uninhibited) and on multiple classes of alloys. Details of the experiments conducted are presented in Table 1.

Corrosion Test Results

Measured corrosion rates from the two experiments were substantially different. Corrosion rates in the 10% acetic acid at 450°F were considered mild, with 316L exhibiting the highest corrosion rate of 242 mpy (6.1 mm/yr). Corrosion rates in the 10% HCl / 10% acetic acid with H_2S environment were extremely high for all alloys except Ta surface-alloyed 316L; 316L, Ti 6-4, and Ti 6-2-4-6 coupons completely dissolved after 8 hours of exposure and the C276 samples were corroded severely.

Results of test #1: 10% acetic acid at 450°F: As expected based on previous investigations in organic acidizing solu-

Materials Testing, *continued*

Table 1 — Experimental conditions for corrosion evaluation in acidizing solutions

Test	Alloys	No. of coupons in liquid	SolutionConcentration	Temperature	Pressure	Duration
1	316L C276 Ti 6-4 Ti 6-2-4-6 Ta-surface alloy	Two per alloy	10% acetic acid	450°F (230°C)	35 psi N_2 applied at 70°F (21°C)	8 h
2			10% acetic acid 10% HCl		15 psia H_2S at 450°F (230°C) 140 psi N_2 at 70°F (21°C)	

tions at high temperature[1-4], corrosion rates ranged from nil to moderate for the alloys evaluated. The tantalum surface alloy and Ti 6-2-4-6 exhibited zero corrosion. The corrosion rate of 316L was 242 mpy (6.1 mm/yr), while corrosion rates on C276 and Ti 6-4 were 11.9 and 2.2 mpy (0.3 and 0.1 mm/yr), respectively. Visually, all of the Ta surface alloyed equipment appeared unaffected by the exposure. Table 2 shows detailed results, and coupons are shown in Fig. 5.

Results of Test #2: 10% HCl / 10% Acetic Acid / 15 psia H_2S at 450°F: Corrosion rates were extremely high for the alloys evaluated except the Ta surface alloy. Ta surface alloy coupons showed no corrosion and were observed to have a blue tint due to plating of metallic ions from solution during the exposure. The 316L, Ti 6-4, and Ti 6-2-4-6 coupons all completely dissolved during the 8 hour exposure (Fig. 6), translating to minimum corrosion rates in the range of 16 to 41 in./yr (406 to 1,049 mm/yr). C276 coupons were severely attacked and the corrosion rate was measured at 21 in./yr (531 mm/yr). Visual inspection indicated that all of the tantalum surface alloyed equipment and associated parts had no signs of corrosive attack. Table 3 shows detailed test results and post-exposure coupons are shown in Fig. 7. The performance of the tantalum surface alloyed coupons, autoclave, and accessories successfully demonstrated the good corrosion protection provided by the Ta surface treatment process in the highly aggressive environments. Inspection of the coupons, autoclaves, and accessories found no indications of localized attack, blistering, or other damage to the tantalum surface alloy or underlying substrate.

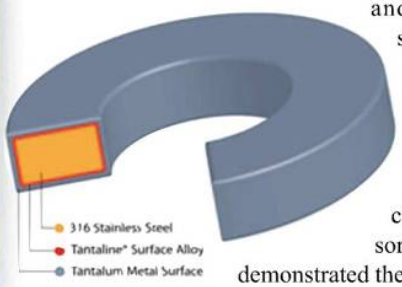

Fig. 3 — *Depiction of tantalum surface alloy on 316SS.*

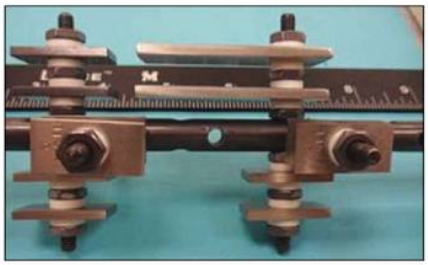

Fig. 4 — *Sample test rack.*

Table 2 — Corrosion rates in 10% acetic acid at 450°F (230°C).

Material	Weight-loss over 8 hour exposure, mg	Corrosion rate, mpy (mm/yr)	Average corrosion rate, mpy (mm/yr)
316L	30.6	193 (4.9)	242 (6.1)
	45.8	291 (7.4)	
C276	2.1	12.2 (0.3)	11.9 (0.3)
	2.0	11.6 (0.3)	
Ti 6-4	0.3	3.3 (0.1)	2.2 (0.1)
	0.1	1.1 (0.0)	
Ti 6-2-4-6	None	0	0
	Nil(-0.1)	0	
Ta surface-alloy	Nil (-0.3)	0	0
	Nil (-0.3)	0	

Table 3 — Corrosion rates in 10% HCl /10% acetic acid / 15 psia H_2S at 450°F (230°C).

Material	Weight-loss over8 hour exposure, mg	Corrosion rate, mpy (mm/yr)	Average corrosion rate, mpy (mm/yr)
316L	Dissolved > 5,787	Dissolved > 36,506 (> 927)	Dissolved > 36,517 (>928)
	Dissolved > 5,747	Dissolved >36,517 (>928)	
C276	3,604	20,901 (531)	20,897 (531)
	3,589	20,893 (531)	
Ti 6-4	Dissolved > 3,733	Dissolved > 41,341 (>1,050)	Dissolved > 41,341 (>1,050)
	Dissolved > 3,718	Dissolved > 41,312 (>1,049)	
Ti 6-2-4-6	Dissolved > 1,260	Dissolved >16,289 (>414)	Dissolved >16,289 (>414)
	Dissolved >1,259	Dissolved > 16,231 (>412)	
Ta-surface alloyed 316L	Nil (-1.7)	0	0
	Nil(-1.7)	0	

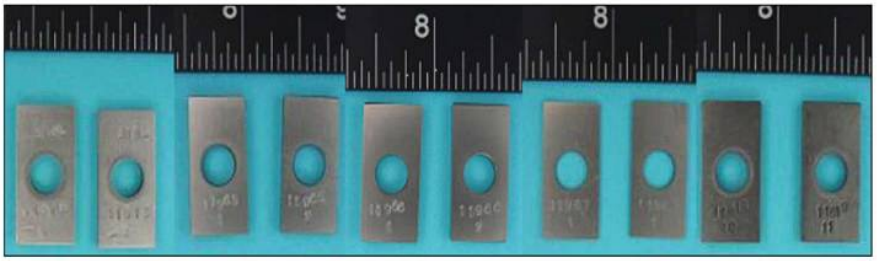

Fig. 5 — *Photographs of coupons following exposure to 10% acetic acid at 450 F. Left to right: 316L, C276, Ti 6-4, Ti 6-2-4-6, Ta surface alloy.*

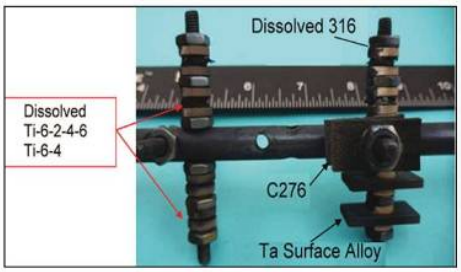

Fig. 6 — *Photographs of specimen test rack following exposure to 10% HCl / 10% acetic acid / 15 psia H_2S at 450°F (230°C).*

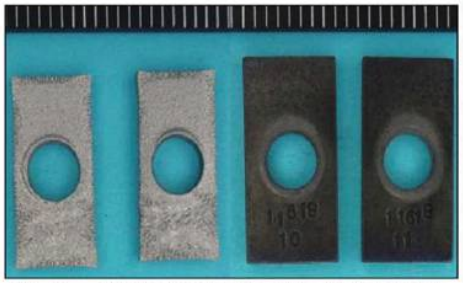

Fig. 7 — *Photographs of coupons following exposure to 10% HCl / 10% acetic acid / 15 psia H_2S at 450°F (232°C). Left to right: C276, Ta surface alloy (other alloy coupons were dissolved).*

Conclusions

In H_2S containing acidizing environments at high temperatures, traditional high-performance corrosion-resistant alloys exhibit severe corrosion attack. This study demonstrates that tantalum surface alloys provide the needed corrosion resistance in deep well environments. With the good corrosion protection, availability, and economics of Ta surface alloys, these materials offer a viable alternative to high-performance corrosion-resistant alloys such as nickel, titanium, zirconium, and solid tantalum. iTSSe

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