

Evaluation of Hydrogen Embrittlement of Nickel-Based Alloys in Cesium Formate with H₂S/CO₂

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ABSTRACT

Because of hydrogen generation from thermal decomposition of cesium formate, there were concerns that the use of cesium formate in certain applications may induce hydrogen embrittlement to CRA equipment after extensive exposure to elevated temperatures followed by cooling to low temperature under stress. This study focused on evaluating the severity of hydrogen embrittlement of seven nickel-based alloys at room temperature following exposure at elevated temperature to cesium formate of H₂S/CO₂ acid gases and consequently reduced pH. Unstressed slow strain rate (SSR) test specimens were previously exposed in an autoclave of cesium formate saturated with H₂S/CO₂ at an elevated temperature of 275 °F for 90 days. After exposure, significant hydrogen uptakes were observed under the tested conditions by measurement of total hydrogen concentration. The hydrogen-charged SSR specimens were then tested in air with 1×10^{-6} in./in./s strain rate at room temperature and compared with performance of the pristine specimens. In addition, three charged CRA alloys were also heated in furnace to release dissolved hydrogen and then tested in air. Two of the seven CRAs were also strained in situ in cesium formate at 275 °F. The SSR results (yield strength, ultimate tensile strength, reduction of area and elongation) at the different test scenarios are compared to identify the hydrogen embrittlement severity. Variation in hydrogen embrittlement susceptibility among the seven CRA alloys were observed. The HE severity did not seem to correlate with the measured total hydrogen concentration but relate to the yield strength of the material to a certain extent. The low yield strength (66 ksi) of alloy 625 is the only outlier which did not suffer from hydrogen embrittlement while the other high strength alloys with YS ranging from 118 ksi to 160 ksi suffered hydrogen embrittlement. The highest yield strength of alloy 945X (159 ksi) exhibited the lowest resistance to hydrogen embrittlement. The hydrogen embrittlement at room temperature also appears to be reversible after thermal removal of hydrogen.

Key words: Cesium Formate, Hydrogen Embrittlement, Total Hydrogen Concentration, SSR Test, Nickel-Based Alloys

INTRODUCTION

Cesium formate (CsFo) brines have been used as the drilling and/or completion fluids in oil and gas wells in need of high-density fluids.^{1,2} Multiple studies on corrosion of steels and corrosion resistance alloys (CRA) in formate environments have been reported in the literature.²⁻⁸ It was known that the formate brines could undergo significant decomposition to form hydrogen when in contact with catalytic surfaces which CRA can act as. Therefore, there have been concerns that the CRA may catalyze the decomposition of formate brines to accelerate the generation of hydrogen which in turn may embrittle certain CRAs and endanger the relevant well equipment.

In this work, the susceptibility of hydrogen embrittlement of seven different CRAs was studied by exposure at elevated temperature to cesium formate brine with H₂S and CO₂ gases and consequently reduced pH, and then evaluating slow strain rate tensile performance at room temperature with supersaturated hydrogen. One CRA was also tested in-situ in the formate fluid at elevated temperature.

EXPERIMENTAL PROCEDURE

Seven different CRAs were studied, namely, alloy 625 (UNS N06625), alloy 625+ (UNS N 07716), alloy 718 (UNS N07718), alloy 725 (UNS N07725), alloy 925 (UNS N09925), alloy 945 (UNS N09945) and 945X (UNS N09945). Each of CRAs were certified to NACE MR0175 and/or API 6A CRA specifications.

Round bar slow strain rate (SSR) test specimens are machined from each material with 0.15" gauge diameter and 1.00" gauge length in accordance with NACE TM0198-2020. The gripping shoulder diameter of the specimens was 0.25".

Three unstressed SSR specimens from each material were first put into an autoclave of cesium formate brine that was charged with 0.2678 mol% H₂S Balance CO₂ at 275°F and exposed for 90 days aiming to charge hydrogen from decomposition of cesium formate to the materials. The alloys of 725/925/945X were charged together in the first autoclave while the remaining alloys of 625/625+/718/945 were charged together in the second autoclave. In both tests, the cesium formate brine was de-aerated with 1 bar research grade CO₂ which consequently reduced the formate pH significantly to pH 8.5 or 7.8 at RT, respectively. The subsequent introduction of H₂S and CO₂ acid gases at 275°F would reduce the pH of cesium formate further though in-situ pH was not measured. For the first autoclave, the starting initial total pressure was 274 psia and the final total pressure at the end of the test was 946 psia. For the second autoclave, they were 270 psia and 1163 psia, respectively. After initial varying pressure increase rate, both tests eventually achieved an approximately steady pressure increase rate, 8.7 psia per day for the first autoclave containing 9 specimens and 12.9 psia per day for the second autoclave containing 12 specimens. Upon removal from autoclave at the end of 90-day exposure, the SSR specimens were stored in liquid nitrogen to avoid hydrogen outgassing while waiting for further testing and analysis. Note that the post-test cesium formate solutions were measured at RT at 1 bar CO₂ and exhibited pH 8.1 and pH 8.3 respectively for the two tests.

One hydrogen-charged SSR specimens from each material was analyzed for total hydrogen concentration by the inert gas fusion thermal conductivity method per ASTM E1447 using LECO Instrumentation. Triplicate analysis samples were taken from the SSR specimen gauge section and shoulder section, respectively. The analysis was also performed similarly on a pristine specimen of each material that was not exposed to cesium formate, which serves as the baseline hydrogen concentration within the material by the same measurement method.

All the SSR tests were performed with a strain rate of 1×10^{-6} in./in./s. They were mostly tested in air at room temperature while a few were tested in situ in cesium formate at 275°F. Each CRA had a pristine SSR specimen tested in air at room temperature. Alloys 625/725/925/945X had duplicate hydrogen-

charged SSR specimens tested in air at room temperature. On the contrary, alloys 625+/718/945 had a single hydrogen-charged SSR specimen tested in air at room temperature and had the second previously hydrogen-charged SSR specimen baked in furnace with air at 400 °F for at least two weeks to release the dissolved hydrogen and then tested in air at room temperature. In addition, alloys 625 and 945 had at least one SSR specimen tested in situ in cesium formate with 0.2678 mol% H₂S Balance CO₂ at 275°F after 7-day presoaking in the same environment. The conditions of SSR test specimens will be identified when discussing the test results of each material.

Stereoscopic images were taken for each SSR specimen. SEM was performed on selected materials (alloy 718, 945 and 945X) to confirm the ductile and brittle failure features on their fracture surface. The comparison between different test conditions were focused on the outer edge of the fracture surface considering that hydrogen enter the materials from the outer surface of the specimen.

RESULTS

Total Hydrogen Concentration

Table 1 lists the hydrogen concentration that was intentionally charged into the 0.15" diameter of gauge section for each CRA. Table 2 lists the hydrogen concentration that was charged into the 0.25" diameter of gripping shoulder section of the SSR specimen of each CRA. Note that both the gauge and shoulder sections of the same SSR specimens had triplicate coupons taken for analysis. The hydrogen concentrations of 625, 625+ and 725 in the gauge section appear to be around 20 ppm and lower than the alloys of 718, 925, 945 and 945X which ranged from 30 ppm to 60 ppm. The hydrogen concentrations of 625, 625+ and 725 in the shoulder section appear to be slightly lower than the gauge section by 2~5 ppm while the difference for alloys of 718, 925, 945 and 945X was more significant by 10~30 ppm. The difference of hydrogen concentration between the gauge and shoulder section was not supposed to be the same unless the hydrogen concentration saturated in the large diameter shoulder section. However, it should be also pointed out that the differentiation seems to coincide with the corrosion conditions on the CRA surface. As reported later, the alloys of 625, 625+ and 725 remained shiny (low hydrogen concentration measured) after the test while the surfaces of the other four alloys covered with corrosion product measured high hydrogen concentration. Note that grinding was performed prior to the hydrogen analysis aiming to remove the corrosion product on the alloys of 718, 925, 945 and 945X to avoid unwanted results. But it is possible that the removal was more complete for the large diameter of shoulder section than the small diameter of gauge section because of the need to conserve necessary analysis mass by the hydrogen analysis lab. In other words, it was not concluded whether the hydrogen concentration has reach solubility within the gauge sections of tested CRAs. But generally speaking, the hydrogen concentration of alloys 925, 945 and 945X seems higher than the alloys of 625, 625+, 725 and possibly 718. Alloy 945 has the higher hydrogen concentration of ~60 ppm in gauge section and ~27 ppm in should section. Alloy 625+ has the lowest hydrogen concentration of ~20 ppm in gauge section and ~16 ppm in the shoulder sections.

Table 1 Total Hydrogen Concentration within the Gauge Section of Pristine Samples and Samples with 90 days of CsFo exposure

H, ppm	Pristine Sample (Not Exposed to CsFo)					After 90-Day Exposure to CsFo					Δ[H]
Sample No.	1	2	3	Average	Std. Dev.	1	2	3	Average	Std. Dev.	
625	4	0.48	0.38	1.62	1.68	26.06	24.3	25.02	25.13	0.72	23.51
625+	0.94	0.42	0.55	0.64	0.22	19.35	22.46	20.02	20.61	1.34	19.97
718	0.26	0.33	0.53	0.37	0.11	31.54	30.98	30.29	30.94	0.51	30.56
725	0.98	0.24	0.59	0.60	0.30	20.71	21.21	20.2	20.71	0.41	20.10
925	2.51	2.78	2.7	2.66	0.11	31.1	30.29	46.92	36.10	7.66	33.44
945	0.49	1.17	1.39	1.02	0.38	57.95	61.62	65.54	61.70	3.10	60.69
945X	0.58	0.21	0.53	0.44	0.16	30.29	49.3	48.54	42.71	8.79	42.27

Δ[H]: The difference in total hydrogen concentration between the CsFo exposed and pristine samples

Table 2 Total Hydrogen Concentration within the Shoulder Section of Pristine Samples and Samples with 90 Days of CsFo Exposure

H, ppm	Pristine Sample (Not Exposed to CsFo)					After 90-Day Exposure to CsFo					$\Delta[H]$
Sample No.	1	2	3	Average	Std. Dev.	1	2	3	Average	Std. Dev.	
625	0.68	1.6	1.07	1.12	0.38	19.5	19.69	17.79	18.99	0.85	17.88
625+	0.78	1.43	1.56	1.26	0.34	17.81	16.54	18.28	17.54	0.73	16.29
718	0.67	0.66	1.12	0.82	0.21	19.8	18.71	20.27	19.59	0.65	18.78
725	1.99	0.86	1.89	1.58	0.51	20.94	17.51	20.3	19.58	1.49	18.00
925	3.77	3.6	3.63	3.67	0.07	22.29	26.74	22.18	23.74	2.12	20.07
945	0.79	1.11	0.93	0.94	0.13	26.7	34.56	23.1	28.12	4.79	27.18
945X	0.99	1.17	1.03	1.06	0.08	23.19	24.36	25.12	24.22	0.79	23.16

SSR Result Summary Table

Table 3 summarizes the yield strength (YS), ultimate tensile strength (UTS), percentage of reduction of area (ROA), percentage of total elongation (EL) and plastic elongation (EL_p) of the baseline SSR tests. Table 4 summarizes the results of hydrogen-charged, hydrogen-discharged and in-situ SSR samples that are normalized to the baseline performance of respective CRA.

Table 3 SSR Test Results of the baseline SSR tests

Material	SSR Baseline Test (in air at RT)				
	YS, ksi	UTS, ksi	ROA	EL	EL_p
625	66.6	128.3	63.9%	55.9%	53.1%
625+	117.9	172.4	60.6%	44.2%	40.1%
718	134.3	177.1	31.6%	26.3%	21.4%
725	132.5	180.0	42.9%	31.6%	27.6%
925	119.7	169.1	37.4%	31.1%	26.4%
945	137.3	167.3	44.1%	29.8%	26.2%
945X	159.3	183.4	47.8%	26.3%	22.5%

Table 4 Normalized SSR results of hydrogen-charged, hydrogen-discharged and in-situ SSR samples.

Sample Conditions	Material	YS	UTS	ROA	EL	EL_p
Hydrogen-Charged Samples	625*	0.98	0.98	0.83	0.97	1.00
	625+	0.98	0.86	0.40	0.37	0.31
	718	0.98	0.90	0.48	0.40	0.27
	725*	1.01	0.88	0.41	0.32	0.24
	925	0.98	0.95	0.58	0.66	0.60
	945	0.99	0.93	0.47	0.40	0.31
	945X*	0.99	0.94	0.31	0.26	0.13
Hydrogen-Discharged Samples	625+	1.00	1.00	1.03	0.97	0.97
	718	0.99	1.00	1.20	1.08	1.11
	945	0.99	1.00	1.10	1.04	1.06
In-situ Tested Samples	625	0.70	0.92	0.94	1.10	1.10
	945	0.91	0.89	0.59	0.66	0.60

Note: * indicates average data of duplicate tests. Otherwise, data is from a single test.

Alloy 625 SSR Results

Figure 1 shows the SSR results of alloy 625 that were tested under three sample conditions. The duplicated SSR curves of the hydrogen-charged specimens were reproducible and were similar to the pristine sample that were not exposed to cesium formate for intentional charge of hydrogen. As shown in Table 3, alloy 625 has the following baseline properties: 66.6 ksi YS, 128.3 ksi UTS, 63.9% reduction of area (ROA), 55.9% total elongation and 53.1% plastic elongation. For comparison, the properties of duplicate hydrogen-charged specimens were averaged and normalized to the baseline properties and reported in Table 4. They have essentially the same YS, UTS and total/plastic elongation (at least 97%). The ROA of the hydrogen charged specimens was 83% of the baseline property. Figure 2 shows the appearance of gauge sections of the SSR specimens. Necking was observed for all the test conditions suggesting the ductile failure of the specimens. Therefore, despite the 23.5 ppm hydrogen within the gauge section (see Table 1), the hydrogen-charged alloy 625 did not suffer from premature brittle failure. The in-situ SSR test of alloy 625 also confirmed the absence of hydrogen embrittlement. Although it has a lower yield strength at elevated temperature than room temperature, it did not exhibit decline in elongation. As shown in Figure 2, the alloy 625 samples did not exhibit corrosion product on its surface.

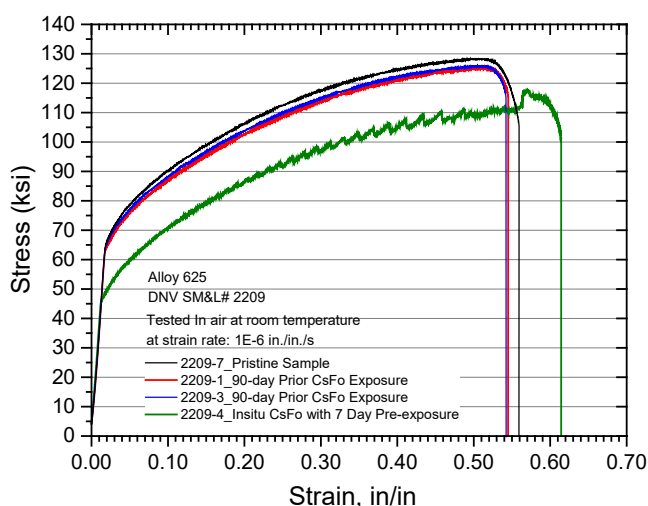


Figure 1: Stress-strain curves of alloy 625 SSR tests at 1×10^{-6} in./in./s strain rate for three sample conditions: (1) a pristine sample tested in air at RT; (2) two samples tested in air at RT that were previously exposed to 275°F CsFo of 0.29 psia f_{H_2S} and 225 psia f_{CO_2} ; (3) one sample tested insitu at 275°F in CsFo of 0.29 psia f_{H_2S} and 225 psia f_{CO_2} with 7-day pre-soaking in the same environment.

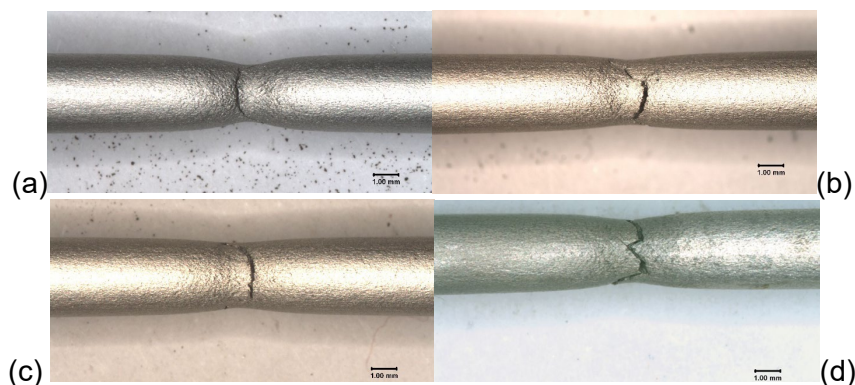


Figure 2: Images of post-test SSR samples of alloy 625: (a) for the pristine sample; (b,c) for the test samples (DNV #2209-1 & 3) that were previously exposed to 275°F CsFo of 0.29 psia f_{H_2S} and 225 psia f_{CO_2} . (d) for the in-situ sample (#2209-4) tested at 275°F in environment.