

ON THE EVALUATION OF PRECIPITATION HARDENING ALLOY 625

FOR USE IN THE PRODUCTION OF SOUR GAS

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Abstract

Natural gas production from reservoirs with high partial pressures of H₂S (i.e., sour) can economically be pursued using high strength, corrosion resistant alloys that have a high resistance to fracture and environmentally assisted cracking. For thick-walled components, development of age hardenable versions of Alloy 625 were required. Several of these have been evaluated in laboratory tests designed to reveal their suitability for use in the production of sour gas. While the compositions and processing steps of these alloys were quite similar, differences in fracture toughness and resistance to hydrogen embrittlement were observed.

Background Information

Corrosion resistant alloys (CRA's) have been used in oil and gas production equipment for many years. Earlier, these alloys were primarily used in valve stems and seats, choke internals, downhole safety and control devices - applications where sealing surfaces are paramount and where even small amounts of corrosion could prevent proper operation. Acid gases, H₂S and CO₂, in the production fluids promoted corrosion. A draft industry Recommended Practice [1] in the mid-60's listed the AISI-300 and 400 series stainless steels, the Monels, Alloy X-750, cold drawn Alloy 600, and the Stellites and Colmonoys as generally satisfactory. No processing restraints except for several specific limitations on hardness were advised. Occasional field cracking failures were reported. Inhibition remained the primary method of corrosion abatement and was tailored to protect the carbon and low alloy steel components in the wells, not the CRA's.

In the early to mid-70's, two developments had a noteworthy impact on CRA usage. Firstly, the exploitation of very corrosive acid gas reservoirs challenged the available inhibitors for steel and forced the consideration of CRA casing and tubing. Alloy 625 (UNS N06625) was one of the three leading candidates for casing with high strength achieved by cold reduction. Age hardening of the cold worked pipe provided a small increment in strength.

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The second development that influenced CRA usage was the adoption of metal-to-metal seals to replace elastomers for most of the prime sealing surfaces including pipe-to-pipe, hanger-to-hanger body spools, packers, and valve stems. In an all CRA system, inhibition is not used and the prevention of corrosion at seal surfaces becomes a more critical issue. Alloy 718 replaced Alloy X-750, because it had more corrosion resistance, in those applications - hangers, packers, stems, etc. - where the thick cross-sections prevented effective cold working to achieve the necessary strength. Attending its adoption, Alloy 718 carried stringent processing controls because high notch toughness was deemed desirable and alternate processing routes for this alloy exploited its creep rupture properties at the neglect of toughness.

CRA's tailored to a particular field environment became an accepted materials selection practice by the 1980's. Corrosion resistance combined with high strength was more readily available in cold worked systems than in age hardened systems. It was recognized that an alloy with more corrosion resistance than Alloy 718 was needed for certain reservoirs in the development of the Mobile Bay, Alabama gas fields. Alloy 625 had the corrosion resistance, but the small increment of strength by aging could not assure the \approx 120 ksi (827 MPa) needed in a number of wellhead and downhole components. With this in mind, a directed effort was started to encourage a number of alloy suppliers to develop a new alloy or enhance the existing Alloy 625 to meet these needs.

This paper presents the laboratory test results performed on candidate materials obtained from various suppliers in the form of bar stock with a relatively large cross-section intended for hanger, packer body, and wellhead component applications. They are offered in the hope that further development toward optimum performance will be pursued by interested parties.

Materials Evaluation

Materials

Precipitation hardened (PH) Alloy 625 is a modification of Alloy 625 that permits strengthening by aging in significantly shorter times than can be achieved with Alloy 625. The strengthening occurs by the precipitation of γ'' ($\text{Ni}_3\{\text{Nb},\text{Ti},\text{Al}\}$); little or none of γ' ($\text{Ni}_3\{\text{Ti},\text{Al},\text{Nb}\}$) is present [2,3]. Strengthening by precipitation hardening is preferred to the cold working of CRA's for the case of high strength, thick-walled products because it produces more uniform through-wall mechanical properties.

Samples of age hardenable Alloy 625 were received from various vendors in solution annealed, solution annealed and aged conditions, or without any heat treatment. Samples of the solution annealed and without heat treatment were subjected to various heat treatments designed to achieve specific properties.

Table 1 is a list of the compositions of the materials reported here. In general, the variables are C and "hardener elements" such as Nb, Ti, and Al. An earlier version of Alloy 625 was subjected to exploratory heat treatments and tested. The results are shown in Table 2. The desired aims of 120 ksi (827 MPa) yield and 40 ft-lbs Charpy impact values were met by specific heat treatments. However, the microstructure showed mixed grain size and "necklace" structure, and required long aging times. These results indicated that alloying modifications as well as heat treatment were necessary to achieve properties within reasonable aging cycles.

Table 3 shows the results for samples with composition modifications to Alloy 625 and different heat treatments. The yield strengths of these materials were \approx 120 to 140 ksi (827 to 965 MPa); the hardnesses were HRC 35 to 40.

Environmental Cracking Studies

Experimental Procedures

Some of the experiments were designed to evaluate PH 625 with respect to its resistance to stress corrosion cracking (SCC), whereas others were designed to reveal susceptibility to hydrogen embrittlement (HE). In all cases, the environmental exposures occurred in deaerated, aqueous NaCl solutions with cover gases added at test temperature. Test duration varied from 30 days to 3 months.

In the case of the SCC tests, C-ring and DCB specimens were exposed to high temperature environments. The C-rings were artificially creviced by spot welding small strips of Alloy C-276 to the O.D. surface at the C-ring apex. C-rings were stressed to the yield strength of the respective materials.

DCB's and C-rings were the specimens studied for resistance to HE also and were coupled to carbon steel throughout the experiments. Two types of HE tests were conducted: 1) room temperature ("cold charging") exposure to either a NaCl solution with a cover gas of H₂S and CO₂ or to the standard NACE TM0177 solution [4] (5wt.% NaCl + 0.5wt.% acetic acid with a cover gas of one atmosphere of H₂S); and, 2) high temperature ("hot charging") exposure to a NaCl solution with a cover gas of H₂S and CO₂ for one month followed by a one month exposure at 250°F and/or to room temperature without opening the autoclave. In several cases the high temperature exposures preceded exposure to NACE solution. The latter more closely resembles some of the conditions that could be experienced by a tubing hanger or sub-surface safety valve if coupled to a steel in sour service.

The DCB's were fatigue pre-cracked then wedge-open loaded; a "target" value of 50 to 70 ksi/in (55 to 77 MPa/m) as used for the initial stress intensity (K_{Ii}). Experimental details for C-rings and DCB's can be found elsewhere [5]. In the high pressure tests, the specimens were not isolated from the Hastelloy C-276 autoclave unless the test involved cathodic polarization by coupling to carbon steel; in these tests the specimens were wrapped in a Teflon net for isolation. The NACE tests were performed in glass vessels.

At the conclusion of each test, each specimen was examined for cracking and localized corrosion. The DCB specimens were broken open so that a complete examination of the fracture surface could be conducted. The final stress intensity values (K_{Ifinal}) for each DCB were determined by measuring lift-off loads and final crack lengths. Values of K_{Ifinal} can be different than the "target" value even when no crack growth occurs because of the accuracy of the set up equations. The actual K_{Ifinal} is calculated using the lift-off load and is considered the more accurate method.

Results

None of the C-ring specimens experienced SCC or HE regardless of exposure conditions. In the SCC tests no localized corrosion was observed under the

artificial crevices on the C-rings or at any other locations on any of the specimens; general corrosion was "negligible".

The values of $K_{I\text{final}}$ in the DCB's varied widely in the HE tests. Values from 35 to 64 ksi/in (38 to 70 MPa/m) were obtained.

The results of the environmental exposure tests are summarized in Table 4.

Discussion of Results

Work performed prior to that reported here studied several early versions of PH 625 [6]. This study showed that no SCC occurred in C-rings exposed to an environment of 25 wt.% NaCl + 0.1 g/l S^o with a cover gas of 2000 psi H_2S at 425°F; the yields of these materials were between 76 and 126 ksi (524 and 869 MPa). However, similar to the results here, DCB specimens showed susceptibility to HE with crack growth producing values of $K_{I\text{final}}$ 31 to 73 ksi/in. Nevertheless, the results indicated promise for Mobile Bay service. SCC had been induced in an aged Alloy 625 in high temperature sour brines containing acetic acid [7].

In the present study, the higher strength versions of PH 625 showed resistance to both SCC and localized corrosion when subjected to simulated, top of well, very sour conditions for 2 months. Under the conditions tested, the threshold stress intensity for SCC is ≥ 49 ksi/in (54 MPa/m) for each version studied (as no crack advance was observed); stresses at yield did not initiate SCC or HE in C-rings.

However, as shown in Table 4 HE occurs to varying degrees among the PH 625 versions studied. Charging temperatures and H_2S partial pressures did not seem to have a great effect on the results; the NACE solution provided as severe an environment as did very high H_2S pressures whether hot and/or cold charging was used. In general, those products with the lowest values of $K_{I\text{final}}$ also were those with the lowest values of Charpy impact and conversely so. Compositions and processing parameters known to us do not give clues regarding the reasons for these varied responses (Charpy and HE). It is not yet clear why these differences exist; this is a subject that requires further study, especially by suppliers of these alloys.

References

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Table 1: Compositions of the Versions of Precipitation Hardened Alloy 625 Studied and Their UNS Limits

<u>Compositions of Materials Studied</u>																
<u>Materials Information</u>				<u>Composition, Element by Wt.% (a)</u>												
<u>WRC X#</u>	<u>UNS No.</u>	<u>C</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Mn</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Ti</u>	<u>Al</u>	<u>Nb</u>	<u>Fe</u>	<u>Cu</u>	<u>Co</u>	<u>N</u>
6086	N06625*	0.049	21.10	Bal	8.35	0.02	0.02	0.007	0.001	0.31	0.34	3.97	4.24	--	0.02	---
6839	N07716	0.009	21.03	60.84	7.96	0.03	0.03	0.007	0.002	1.31	0.18	3.39	5.18	--	--	---
6551	N07716	0.021	19.90	61.45	8.98	0.03	0.08	0.003	0.002	1.27	0.16	3.11	4.92	--	--	---
6912	N07716	0.016	19.18	61.97	9.27	0.13	0.03	0.012	0.002	1.36	0.22	3.53	4.17	--	0.03	---
6746	N07626	0.021	20.49	59.9	8.68	<0.10	0.06	<0.011	---	<0.05	0.53	4.87	5.17	--	<0.06	---
6910	N07725	0.01	20.75	57.1	7.91	0.07	0.04	---	---	1.43	0.24	3.43	9.02	--	--	---
<u>UNS Composition Limits on PH 625 Alloys Studied Compared to Alloy 625:</u>																
	N06625	0.10*	20/23	Bal.	8/10	0.50*	0.50*	0.015*	0.015*	0.40*	0.40*	3.15/4.15	5.0*	--	--	---
	N07716	0.03*	19/22	59/63	7/9.5	0.20*	0.20*	0.015*	0.010*	1/1.6	0.35*	2.75/4.0	Bal.	--	--	---
	N07626	0.05*	20/23	Bal.	8/10	0.50*	0.50*	0.020*	0.015*	0.60*	0.4/0.6	4.5/5.5	6.0*	0.5*	1.0*	0.05*
	N07725	0.03*	19/22.5	55/59	7/9.5	0.35*	0.20*	0.015*	0.010*	1/1.7	0.35*	2.75/4.0	Bal.	--	--	---

(a) Values marked with an asterisk are the maxima permitted under the UNS number designated.

Table 2: Effect of Heat Treatment on Mechanical Behavior of Alloy 625

ID	HEAT TREATMENT	HARDNESS AVG HRC	AGED TENSILE PROPERTIES				IMP Ch
			σ_{ys} (ksi)	σ_{uts} (ksi)	El. (%)	RA (%)	
X-6086							
A	Low Temp Anneal : 1500°F/1h/WQ Pre Nucleation : 1200°F/4h/WQ Age : 1200°F/70h/AC*	38	120	166	32	40	
D	Anneal : None Pre-Nucleation : 1300°F/1h/WQ Age : 1200°F/70h/AC	-- 39	140	171	29	51	
E	Anneal : 1675°F/1h/WQ Pre-Nucleation : None Age : 1200°F/96h/AC	25 39	130	167	32	50	
*B	High Temp Anneal : 1675°F/1h/WQ : 1200°F/4h/WQ : 1200°F/70hr/AC	27 31 39	120	163	40	40	
C	Anneal : None Pre-Nucleation : 1200°F/4h/WQ Age : 1200°F/70h/AC	-- 31 38	129	171	41	44	
F	Anneal : 1725°F/1h/WQ Pre-Nucleation : None Age : 1200°F/70h/AC	21 -- 34	112	160	39	50	
G	Anneal : 1700°F/1h/WQ Age : 1250°F/8h/AC	29	101.1	159	40	52.8	

* WQ = Water Quench
AC = Air Cool

Table 3: Mechanical Properties, Product Forms, and Heat Treatments of the Precipitation Hardened Alloys 625 Studied (a)

WRC X-#	Original Product Form	Dimensions of Product	As-Received Condition	Post Forming Heat Treatment	Mechanical Properties				
					σ_{ys} (ksi)	σ_{uts} (ksi)	El. (%)	RA (%)	Charpy (ft-lb)
6839-A	Round	7- $\frac{1}{4}$ " O.D.	HF + SA	1900F/3 hrs/Fan AC 1350F/8 hrs/FC to 1150F 1150F/8 hrs/AC	≈ 134	≈ 184	36	≈ 32	67,
6839-P	Round	C-ring of X#-6839-A then		1900F/2 hrs/AC peak aged 1400F/8 hrs/FC to 1150F 1150F/9 hrs/AC	≈ 140	"Peak aged" condition estimated no tests were conducted			
6551	Round	4.0" O.D.	HF	1800F/4 hrs/WQ 1350F/8 hrs/FC to 1150F 1150F/8 hrs/AC	124	188	35	35	80
6746	Round	6- $\frac{1}{4}$ " O.D.	HIP'd + A	1325F/8 hrs/FC @100F/hr 1150F/8 hrs/AC	ID location 124 OD location 123	174 172	31 29	33 29	43 43
6910	Round	7- $\frac{1}{2}$ " O.D.	HF	1850F/1 hr/WQ ID location 1400F/6 $\frac{1}{2}$ hrs/AC OD location	129 138	177 181	31 22	40 27	33 33
6912	Round	6" O.D.	SA + A	1900F/2 hrs/AC 1375F/8 hrs/FC @25F/hr to.. 1175F/AC	ID location 137 OD location 118	180 167	21 33	23 40	43 58

(a) SA \equiv Solution annealed; A \equiv Age hardened; HF \equiv Hot forged; WQ \equiv Water Quenched; AC \equiv Air Cooled; FC \equiv Furnace Cooled.

Table 4: Summary of Environmental Cracking Experiments Performed Upon PH Versions of Alloy 625

WRC X#-	Specimen Type	Specimen Hardness (HRC)	Experimental Test Conditions						Results (a,b)						
			Initial Loading Conditions	Temp. [NaCl] (°F) (wt.%)	Cover Gases (H ₂ S CO ₂) (psi)		Test Duration	Cracking Observed?	K _{I final} (ksi/in)						
Stress Corrosion Cracking Test Results:															
6839-A	C-ring	37/38	133 ksi	350	25	200	400	2 mos.	0/1	N/A					
6839-A	DCB	37/39	≈65 ksi/in						0/1	60					
6839-P	C-ring	37/38	140 ksi						0/1	N/A					
6746 OD	C-ring	35/36	124 ksi						0/2	N/A					
6746 OD	DCB	35/36	≈55 ksi/in	350	25	200	400	2 mos.	0/1	54					
6910	C-ring	37/38	133 ksi	350	25	200	400	2 mos.	0/2	N/A					
6910	DCB	37/39	≈50 ksi/in						0/1	50					
6912	C-ring	36/37	128 ksi						0/2	N/A					
6912	DCB	36/37	≈50 ksi/in						0/1	49					
Hydrogen Embrittlement Test Results: (c)															
6910	DCB	37/38	≈70 ksi/in	75	5 (d)	15	-0-	1 mo.	2/2	35, 38					
6912	DCB	36/37	≈70 ksi/in						2/2	36, 37					
6746	DCB	35/36	≈70 ksi/in						2/2	38, 52					
6839-A OD	DCB	37/38	≈70 ksi/in						1/1	50					
6839-A	DCB	37/38	≈70 ksi/in	75	5 (d)	15	-0-	1 mo.	1/1	64					
6551	DCB	38/39	≈60 ksi/in						0/1	60					
6839-A	DCB	37/40	≈60 ksi/in	68	25	200	400	2 mos.	1/2	47, 59					
6839-A	C-ring		133 ksi	325	25	1500	60	1 mo. (e)	0/1	N/A					
6839-A ID	C-ring		140 ksi						0/1	N/A					
6746	C-ring		124 ksi						250	25	≈1000	≈40	1 mo. (e)	0/2	N/A
6910	C-ring	37/38	133 ksi						75	5 (d)	15	-0-	1 mo.	0/2	N/A
6912	C-ring	36/37	128 ksi						0/1	N/A					
6839-A	DCB	37/39	≈60 ksi/in	350	25	200	400	1 mo. (e)	0/1	59					
6551	DCB	36/37	≈60 ksi/in	68	25	≈130	≈260	1 mo.	0/1	60					
6551	DCB	38/39	≈60 ksi/in						1/1	47					

- (a) Results are number of specimens cracked/of number of specimens tested.
- (b) Values for K_{I final} were obtained using lift-off load.
- (c) All HE specimens were coupled to carbon steel throughout the experiment.
- (d) TM0177 solution; also contained 0.5 wt.% of acetic acid.
- (e) The autoclave was cooled to next temperature and test continued. The pressures of the gases decreased.