A NEW AGE-HARDENABLE CORROSION RESISTANT

ALLOY FOR DEEP SOUR GAS WELL SERVICE

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ABSTRACT

Alloy 725 (UNS N07725) is a highly corrosion resistant alloy capable of being age-hardened to 0.2% yield strengths from 115 to 140 ksi (793 to 965 MPa), while maintaining a high level of ductility and toughness[1]. As alloy 725 is an austenitic nickel base alloy which is strengthened by precipitation of a gamma double-prime (γ") during aging, large section sizes can achieve uniform hardening throughout the cross section. The alloy is resistant to pitting and stress corrosion cracking (SCC) in Deep Sour Gas Well environments containing NaCl, H_2S and S at temperatures up to about 450° to 500°F (232° to 260°C), and to sulfide stress cracking (SSC) in the NACE TM-0177 environment. Alloy 725 also exhibits excellent corrosion resistance to other commercially significant environments, such as seawater and mineral acids.

INTRODUCTION

The trend in oil and gas production has been toward deeper wells, enhanced recovery methods and offshore field exploration. Deeper wells and enhanced recovery methods, such as steam injection, in-situ combustion and CO_2 injection, result in hostile environments due to increased temperatures, pressures and environmental H_2S and CO_2 and chloride content. For several decades there has been a need to develop new materials for use in production of oil and gas[2]. Much of the research has centered around the need for high strength Corrosion Resistant Alloys (CRA's) that can withstand the high temperature, high pressure, corrosive oil field production environments. INCONEL alloy 625 (UNS N06625) and INCO alloy C-276 (UNS N10276) have the necessary corrosion resistance, but can only be strengthened through cold work and the desired section sizes are too large to be produced on normal cold working equipment. Age-hardened alloys such as INCONEL alloy 718 (UNS N07718) and INCONEL alloy X-750 (UNS N07750), have been used in these applications but have insufficient corrosion resistance in the most severe environments[3]. INCONEL alloy 725 (UNS N07725) is a highly corrosion resistant alloy which can be age-hardened by precipitation of gamma double-prime [Ni_3 (Nb, Ti, Al)] to yield strength levels of 120 ksi (827 MPa) and above, as desired for deep sour gas well applications. As mentioned, age

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alloy 725 exhibits excellent corrosion resistance to seawater and mineral acid environments, equivalent to annealed alloy 625.

PROCEDURE

Materials for testing came from commercially produced tubing, round rod and sheet. The nominal compositions of the alloys are given in Table 1. Materials were tested either as-produced or solution annealed to obtain suitable structures before aging. Yield strengths were in the 117 to 139 ksi (807 to 958 MPa) range obtained by aging alloy 725 and 718, and in the 127 to 168 ksi (876 to 1158 MPa) range obtained by cold drawing alloys 625 and C-276. C-rings were prepared from tubing and were stressed to 100% of the 0.2% Yield Strength as per ASTM Standard Practice G38. The specimens were finished to a 120 grit surface finish using aluminum oxide paper.

Sulfide Stress Cracking (SSC) Tests

Tests were conducted on steel coupled C-rings in the NACE TM-01-77[4] environment for 720 to 1000 hours of exposure.

Stress Corrosion Cracking (SCC) Tests

C-rings were exposed to 3.2 liters of corrodent contained in a 4 liter autoclave at temperatures from 350°F (177°C) to 500°F (260°C). The specimens were suspended from a TFE fluorocarbon coated rack in the autoclave so that electrical isolation was maintained. The C-rings were exposed for 14 days at 350°F (177°C). At the end of the 14 day test period, specimens were removed and examined for SCC. If no SCC was observed, the temperature was raised 25°F or 50°F and the C-rings were again exposed to the environment (a fresh solution). The 14 day exposures were continued until SCC was observed or the material was tested at 500°F (260°C).

Crevice Corrosion Tests

Crevice corrosion tests were conducted (1) on sheet and strip in flowing seawater at 30°C for 30 days using an acrylic plastic crevice torqued to 25 in.-lbs. (2.9 Nm) and (2) on welded and machined tubing with flowing seawater on the I.D. surface at a mean temperature of 14.4°C $\pm$ 4.4°C for 180 days using a vinyl sleeve secured by clamps to join sections of tubing. This sleeve-joint acts as a crevice former on the O.D. of the tube.

Mineral Acid Tests

Immersion tests were performed in unsaturated, non-deaerated solutions of reagent grade mineral acids. Sheet specimens were ground to a 120 grit surface finish with aluminum oxide paper and cleaned with 1,1,1-trichloroethane just prior to testing. Mass loss corrosion rates were determined in mpy (1 mpy = 0.025 mm/y).

RESULTS AND DISCUSSION

Mechanical Properties

As mentioned, alloy 725 is an austenitic nickel base alloy which is strengthened by precipitation of a gamma double-prime [$Ni_3(Cb, Ti, Al)$] during aging. A solution anneal of 1900°F

± 25°F (1024°C to 1052°C) air cooled or water quenched, is required to put the material in the proper condition before aging. Tables 2 to 7 display various room temperature tensile (RTT), charpy-v-notch (CVN), hardness (HD) and grain size properties for alloy 725 tubing and rod products. While other age-hardening treatments will strengthen the alloy, a 1900°F anneal followed by a dual age of 1350°F/8h, Furnace Cool (FC) at 100°/h to 1150°F/8h/Air Cool (AC) was found to provide the best combination of strength and toughness.

The effect of aging treatment on hardness and room temperature tensile properties of 0.217 in. (5.51 mm) x 2.375 in. (60.3 mm) outside diameter (O.D.) tubing is shown in Table 2. Yield strengths of 128 to 133 ksi (883 to 917 MPa) along with high ductility were obtained by dual aging after anneal of the cold drawn tubing.

For 0.562 to 6 inch (14.3 to 152.4 mm) hot finished round rod in the 1900°F mill annealed condition, Table 3, yield strengths of 125 to 137 ksi (862 to 945 MPa) along with high ductility were observed. For rod of 3 to 6 inch (76.2 to 152.4 mm) diameter, similar strengths and ductilities were observed for longitudinal and transverse orientations.

After a 1900°F anneal and 1350°F dual age, Table 4, round rod which had been cold worked (drawn) 12, 22 and 32% showed no effect of degree of cold work on strength or ductility. For round rod cold worked 12%, Table 5, no effect of annealing temperature (1850° to 1900°F) was observed on room temperature tensile properties when tested in the 1350°F dual aged condition. Slightly higher impact properties were obtained for material annealed at 1875° or 1900°F before aging.

Table 6 displays room temperature tensile data for 7.5 inch (190.5 mm) round rod annealed at 1875 and 1900°F before aging at 1400°F/6h. No effect of annealing temperature on mechanical properties was discernible. Similar strengths and ductilities were observed for center, mid-radius and edge in both longitudinal and transverse orientations. Yield strengths were in the 117 to 123 ksi (807 to 848 MPa) range with the material showing excellent ductility.

Fracture toughness was determined for 5- and 6-inch (12.5 and 15.24 cm) diameter round rod of alloy 725 in the 1350°F dual aged condition. KEE values of 274 to 314 ksi•in$^{1/2}$ were obtained at 0°F(-17.8°C).

Table 7 shows the grain size for as-forged, annealed, and annealed plus aged 7.5 inch (190.5 mm) round rod. Little difference in grain size is observed between the center, mid-radius and edge of the large diameter rod.

Corrosion Testing

Table 8 contains sulfide stress cracking (hydrogen embrittlement) data for steel coupled nickel alloy C-rings evaluated in various heat treated conditions in the NACE TM-0177 environment. For alloy 725, material representing yield strengths up to 139 ksi (958 MPa) and hardnesses up to 40 HRc did not crack when coupled to carbon steel for 720 to 1000 hours. Alloy 718, yield strength 130 ksi (896 MPa) and hardness HRc 34, did not crack in 720 hours of exposure.

Stress corrosion cracking data for C-rings evaluated in a 25% NaCl + 0.5% acetic acid + 120 psig H_2S + 1 g/L sulfur environment is displayed in Table 9. This autoclave environment was designed to simulate conditions in severe deep sour gas wells. Alloy 725 was resistant to SCC up to 450 to 500°F (232 to 260°C). Alloy 718, age-hardened to 130 ksi (896 MPa) yield strength, cracked at

275°F (135°C) in this environment. Cold-drawn alloy 625, yield strength 144 to 160 ksi (993 to 1,103 MPa), cracked at 375°F (191°C). And, cold-drawn alloy C-276, yield strength 127 to 168 ksi (876 to 1,158 MPa), resisted SCC up to about 500°F (260°C). As a result of excellent stress cracking resistance, alloy 725 (N07725) in the solution annealed plus aged condition (HRc 40 maximum) has been included in the NACE MR-0175 document.

Table 10 is a summary of crevice corrosion test data for alloy 625 and alloy 725 sheet specimens, evaluated in flowing seawater at 30°C for 30 days using an acrylic plastic crevice torqued to 25 in.-lbs. (2.9 Nm). Alloy 625 suffered significant corrosion, with a large percentage of the crevices attacked up to a maximum depth of 0.66 mm. In the 1850°F/1h/WQ + 1375°F dual aged condition, alloy 725 exhibited excellent crevice corrosion resistance, with no attack observed in the 30 day exposure.

A summary of crevice corrosion test results for alloy 625 and alloy 725 tube sections, evaluated with flowing seawater on the inside surface (I.D.) of tubes is shown in Table 11. Vinyl sleeves which connected the tube specimens provided crevice formers in the seawater environment. The triplicate alloy 625 specimens initiated crevice corrosion in 1 to 30 days, which penetrated to a maximum depth of 0.12 mm in 180 days of exposure. For the duplicate alloy 725 specimens in the 1375°F dual aged condition, only one specimen was attacked, with a maximum penetration of 0.01 mm in 180 days.

Corrosion results for alloy 725 in mineral acids, compared to alloys 625 and C-276 are shown in Table 12. In all of the mineral acid environments of this study, both annealed and annealed plus aged alloy 725 exhibited corrosion resistance comparable to mill annealed alloys 625 and C-276.

CONCLUSIONS

(1) Alloy 725 (UNS N07725) is an austenitic nickel based alloy strengthened by precipitation of gamma double-prime during aging. Depending on the mill form, 0.2% Yield strengths from 117 to 137 ksi (807 to 945 MPa) were obtained by dual aging after annealing. Excellent ductility and toughness properties were retained following age-hardening.

(2) Stressed C-rings of alloy 725 resisted sulfide stress cracking (hydrogen embrittlement) in the NACE TM-0177 environment, stress corrosion cracking in environments containing NaCl, H_2S and S at high pressures and at temperatures up to 450 to 500°F (232 to 260°C).

(3) The corrosion resistance of alloy 725 is similar to that of cold-worked alloy 625 (UNS N06625) and is superior to that of age-hardened alloy 718 (UNS N07718).

(4) Alloy 725 is resistant to pitting and crevice corrosion by seawater and to general corrosion in various mineral acid environments.

REFERENCES

(1) Hibner, E.L., "A New Age-Hardenable Corrosion Resistant Alloy for Deep Sour Gas Well Service," CORROSION/90, April 23-27, 1990, Paper No. 50.

(2) Kane, R.D., *International Metals Reviews*, Vol.30, No.6, p.291, 1985.

(3) DeBold, T.A. and Frank, R., *Materials Performance*, Vol. 27, No. 9, p.59, September, 1988.

(4) Standard TM-01-77, "Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures," National Association of Corrosion Engineers, Houston, TX 1986 revision.

(5) As communicated by the Department of the NAVY, Naval Sea Systems Command, Washington, DC 20362-5101.

Table 1. Chemical Composition (wt.%)

	Alloy 725 *(UNS N07725)*	Alloy 625 *(UNS N06625)*	Alloy 718 *(UNS N07718)*	Alloy C-276 *(UNS N10276)*
Ni	57	65*	52.5	59*
Cr	21	21.5	19	15.5
Mo	8	9	3	15.5
Nb	3.5	3.5	5.1	–
Ti	1.5	–	0.9	–
Fe	9*	–	19*	5
W	–	–	–	4

* Balance element, approximate composition.

Table 2. Room Temperature Tensile Properties for Alloy 725 (UNS N07725) Cold-Drawn* 0.217in.(5.51mm) Wall x 2.375in.(60.3mm) O.D. Tubing

Anneal	Age	HD (RC)	0.2% YS (ksi)	TS (ksi)	El (%)
1850°F	1375°F Dual Age	40	128	184	28
1875°F	1375°F Dual Age	39	132	183	28
1900°F	1375°F Dual Age	39	133	183	27
1900°F	1350°FDual Age	38	133	185	30

°C = 5/9 (°F - 32); 1 ksi = 6.89 MPa

* Cold-Drawn 17%; Longitudinal Properties Given.

Heat Treatment:

ANNEAL = Temp. °F/1h/Water Quench

DUAL AGE = Temp. °F/8h, Furnace Cool 100°/h to 1150°F/8h/Air Cool

Table 3. Room Temperature Tensile Properties for Alloy 725 (UNS N07725) Hot Finished Round Rod in the 1900°F Mill Annealed + 1350°F/8h, FC at 100°/h to 1150°F/8h/AC

Rod Diameter	Orientation	0.2% Y.S. (ksi)	T. S. (ksi)	El (%)	RA (%)	HD (Rc)
0.562 inch	longitudinal	126	179	37	45	34/36
1	longitudinal	129	188	29	46	36/38
3	longitudinal	135	181	30	43	37/38
3	transverse	137	187	27	35	
4	longitudinal	132	174	33	47	33/36
4	transverse	134	178	31	35	
5	longitudinal	132	181	31	45	36/39
6	longitudinal	130	182	29	44	35/37
6	transverse	125	175	31	38	

(1 in. = 25.4 mm; 1 ksi = 6.89 MPa)

Table 4 . Room Temperature Tensile Properties for Alloy 725 (UNS N07725) Cold Drawn Round Rod in the 1900°F/1h/WQ +1350°F/8h, FC at 100°/h to 1150°F/8h/AC

Diameter	% Cold Work	0.2% Y.S. (ksi)	T.S. (ksi)	El (ksi)	RA (%)	HD (Rc)
1.341 inch	12	127	180	31	47	39
1.270 inch	22	127	180	32	48	39
1.187 inch	32	127	179	33	47	37

(1 in. = 25.4mm; 1 ksi = 6.89 MPa)

Table 5. Room Temperature Tensile and Charpy-V-Impact Properties for Alloy 725 (UNS N07725) Cold Drawn* 1.341 Inch Round Rod

Anneal	Condition	0.2% Y.S. (ksi)	T.S. (ksi)	El (ksi)	RA (%)	HD (Rc)	Impact** (ft-lbs)
1850°F	1350°F Dual Age	129	183	29	48	38	58;66
1875°F	1350°F Dual Age	129	182	30	47	39	64;70
1900°F	1350°F Dual Age	127	180	31	47	39	66;69

°C = 5/9 (°F - 32); 1 ksi = 6.89 MPa
*Cold Drawn 12%. **Duplicate specimens.
Anneal = Temp.°F/1h/Water Quench.
Dual Age = Temp.°F/8h, FC at 100°/h to 1150°F/8h/Air Cool.

Table 6. Room Temperature Tensile Properties for Alloy 725 (UNS N07725) Forged 7.5 in. (190.5mm) Round Rod

Condition	Orientation	0.2% Y.S. (ksi)	T. S. (ksi)	El (%)	RA (%)	HD (Rc)
1	long. (mid.-rad)	117	169	32	49	38
1	Trans. (edge)	124	173	30	49	34
1	Trans. (mid-rad)	120	170	34	47	37
2	Long. (edge)	117	171	32	47	37
2	(Long. (mid-rad)	121	169	31	45	38
2	Long. (center)	123	172	35	48	37
2	Trans. (edge)	120	170	31	45	35
2	Trans. (mid-rad)	121	168	36	49	35
2	Trans. (center)	118	168	33	45	36

Condition
1. As-Forged + 1875°F/1h/WQ + 1400°F/6h/AC
2. As-Forged + 1900°F/1h/WQ + 1400°F/6h/AC

°C = 5/9 (°F - 32); 1 ksi = 6.89 MPa

Table 7. ASTM Grain Size for Alloy 725 (UNS N07725) Forged 7.5 in. (190.5mm) Round Rod

	ASTM Grain Size No.		
Condition	Center	Mid-Radius	Edge
As-Forged	6	6	7-1/2
As-Forged + 1900 F Anneal	5-1/2	5	6
As-Forged + 1900°F Anneal + 1375°F/8h, FC at 100°/h to 1150°F/8h/AC	5-1/2	4	5-1/2

°C = 5/9 (°F - 32)

Table 8. Sulfide Stress Cracking Data for Steel Coupled Nickel Alloy C-rings, Evaluated in Various Heat Treated Conditions in the NACE Environment*

			Properties			
Alloy	Condition	Mill Product	0.2% Y.S (ksi)	HRc	Test Duration (hours)	Cracking Yes (Y) or No (N)
725 (N07725)	1	Tubing	139	35	720	N;N
"	1	"	129	40	720	N;N
"	2	"	138	39	720	N;N
"	2	"	132	36	1000	N;N
"	3	"	134	39	1000	N;N
"	4	"	133	38	720	N;N
718 (N07718)	5	"	130	34	720	N;N

* NACE TM-01-77, 5%NaCl + 0.5% Acetic Acid + H_2S saturated at 75°F.

Condition:

(1) 1850°F/1h/WQ + 1375°F/8h, FC 100°/h to 1150°F/8h/AC
(2) 1875°F/1h/WQ + 1375°F/8h, FC 100°/h to 1150°F/8h/AC
(3) 1900°F/1h/WQ + 1375°F/8h, FC 100°/h to 1150°F/8h/AC
(4) 1900°F/1h/WQ + 1350°F/8h, FC 100°/h to 1150°F/8h/A
(5) 1875°F/1h/WQ + 1425°F/8h/AC
°C = 5/9 (°F - 32); 1 ksi = 6.89 MPa

Table 9. C-ring SCC Test Data For Nickel Alloys*, Evaluated at 100%YS in 25% NaCl + 0.5% Acetic Acid + 120psig H_2S + 1 g/L S

			SCC in 14 Days – Yes(Y) or No(N)						
			Temperature (°F)						
Alloy – UNS# (mill form)	**Condi-tion**	**Y.S. (ksi)**	**350**	**375**	**400**	**425**	**450**	**475**	**500**
725 – N07725	1	118	N;N	N;N	N;N	N;N	N;N	N;Y	N
"	2	129	N;N	N;N	N;N	N;N	Y;Y		
"	2	139	N;N		N;N		N;N		N;Y
"	3	133	N;N	N;N	N;N	N;N	N;N	N;Y	N
"	4	132	N;N	N;N	N;N	N;N	N;N	N;N	N;N
"	4	138	N;N		N;N		N;N		N;N
"	5	133	N;N		N;N		N;N		N;N
718 – N07718	6	141	Y;Y**						
625 – N06625	7	144	N	Y					
"	7	160	N	Y					
C-276 – N10276	7	127		N	N	N	N	N	N
"	7	155		N	N	N	N	N	Y
"	7	167		N	N	N	N	N	N
"	7	168		N	N	N	N	N	Y

* Multiple specimens as indicated.
** Alloy 718 cracked at 275°F in this environment.
°C = 5/9 (°F – 32)

Condition:
1. 1850°F/1h/WQ + 1400°F/6h/AC
2. 1850°F/1h/WQ + 1375°F/8h, FC 100°/h to 1150°F/8h/AC
3. 1850°F/1h/WQ + 1400°F/8h, FC 100°/h to 1150°F/8h/AC
4. 1875°F/1h/WQ + 1375°F/8h, FC 100°/h to 1150°F/8h/AC
5. 1900°F/1h/WQ + 1350°F/8h, FC 100°/h to 1150°F/8h/AC
6. 1875°F/1h/WQ + 1425°F/8h/AC
7. As-drawn

Table 10. Summary of Crevice Corrosion Test Data for Sheet and Strip Specimens of Alloy 625 (N06625) and Alloy 725 (N07725), Evaluated in Flowing Seawater at 30°C for 30 Days Using an <u>Acrylic Plastic Crevice</u> Torqued to 25 in.-lbs. (2.9 Nm)

Alloy	Observed Initiation (days)	Percent of Sites Attacked	Maximum Depth of Attack (mm)
625 (N06625)*	2 to 5	25 to 75	0.02 to 0.66 (Average 0.26)
725 (N07725)**	None at 30 Days	0	0.00

* Data for 4 heats of mill annealed commercial sheet.
** Data for 1 heat of hot rolled commercial strip in condition:
1850°F/1h/AC + 1375°F/8h, FC at 100°/h to 1150°F/8h/AC.

Table 11. Summary of Crevice Corrosion Test Data for Specimens of Alloy 625 (N06625) and Alloy 725 (N07725), Evaluated with Flowing Seawater on the I.D. Surface at a Mean Temperature of 14.4°C ± 4.4°C for 180 Days Using Vinyl Sleeves Secured with Clamps as a Crevice Former

Alloy	Observed Initiation (days)	Maximum Depth of Attack (mm)
625 (N06625)*	1 to 48	<0.01 to 0.12
725 (N07725)**	30 (1 specimen only)	0.01 (1 specimen only; second specimen no attack)

* Data for 3 specimens of commercially produced welded tubing.
** Data for 2 machined tube specimens in condition:
1875°F/1h/AC + 1375°F/8h, FC at 100°/h to 1150°F/8h/AC

Table 12. Corrosion Results for Alloy 725 (N07725) in Mineral Acids*, Compared to Literature Data for Alloy 625 (N06625) and Alloy C-276 (N10276)

	Corrosion Rate (mpy)						
Alloy 725 Condition	3% HC1 150°F	5% HC1 150°F	10% HC1 150°F	Boiling 10% H_2SO_4	Boiling 10% HNO_3	Boiling 30% H_3PO_4	Boiling 85% H_3PO_4
1	<1;<1	<1;<1	104;105	19;31	<1;<1	3;3	67;79
2	<1;<1	<1;<1	262;273	20;29	<1;<1	2;7	61;63
3	<1;<1	<1;<1	237;262	20;29	<1;<1	3;3	41;48
4	<1;<1	<1;<1	216;219	23;33	<1;<1	<1;3	24;46
Literature							
Alloy 625	<1	68;70	80-105	18	<1	<10	18-32
Alloy C-276	<5	5-20	20	20	16	<5	5-25

*Duplicate specimens. 1 mpy = 0.0254 mm/y.

Condition:
1. As-mill-annealed
2. As-mill-annealed + 1400°F/6h/AC
3. As-mill-annealed + 1375°F/8h, FC at 100°/h to 1150°F/8h/AC
4. As-mill-annealed + 1350°F/8h, FC at 100°/h to 1150°F/8h/AC

°C = 5/9 (°F - 32)