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Custom Age 625® Plus Alloy—A Higher Strength Alternative to Alloy 625

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Highly corrosion-resistant, age-hardenable alloys are needed in severely corrosive environments such as those encountered in deep sour-gas wells. Age hardenability is important because high strength levels of 827 MPa (120 ksi) minimum 0.2% yield strength are required in large section sizes. Custom Age 625 PLUS was developed to provide higher strength levels than those attainable with alloy 625 along with similar corrosion resistance (more corrosion resistant than alloy 718). The development and metallurgy of Custom Age 625 PLUS are reviewed. The mechanical properties and corrosion resistance of 625 PLUS, 625, and 718 alloys are compared.

1. Introduction

HIGHLY corrosion-resistant alloys are needed for production of deep sour-gas wells. Age-hardenable alloys are desirable because high strength levels can be obtained in large section sizes (greater than 102-mm or 4-in. diameter), which are very difficult to strengthen by cold or warm working. Existing age-hardenable nickel-base alloys such as alloys 718 and X-750 have insufficient corrosion resistance in the most severe environments that contain chlorides and sulfides at high pressures and temperatures up to about 232 °C (450 °F). Nickel-base alloys 625 and C-276 have excellent corrosion resistance, but must be cold worked to obtain high strength levels.

Custom Age 625 PLUS alloy was developed to combine the excellent corrosion resistance of alloy 625 with an age-hardening capability similar to that of alloy 718. This article summarizes the development and metallurgy of 625 PLUS alloy including the mechanical properties and corrosion resistance. Other presentations are covered in Ref 1 through 4.

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*5% NaCl + 0.5% acetic acid purged with H_2S.

2. Alloy Development/Composition

A nickel-base alloy with high levels of chromium and molybdenum is required to resist pitting corrosion, crevice corrosion, and stress-corrosion cracking (SCC) in chloride/sulfide-containing environments such as those encountered in deep sour-gas wells. Additions of niobium, titanium, and aluminum could be used to promote age hardening. However, the alloy would require a critical balance of these elements to provide high strength and excellent corrosion resistance without precipitation of deleterious phases.

Corrosion tests used to evaluate experimental compositions included pitting and crevice corrosion tests in chloride environments, sulfide-stress-cracking tests in the NACE TM0177 environment* (steel coupled at ambient temperature), and chloride-stress-cracking tests at 155 °C. In addition, the alloys were evaluated for SCC resistance in a simulated deep-well environment containing 25% NaCl, 0.5 g/l elemental sulfur, and 9.7 MPa (1400 psig) H_2S at 204 to 260 °C (400 to 500 °F). Stressed samples were exposed for 4 to 6 weeks in autoclaves. Room-temperature tensile properties, Charpy V-notch impact toughness, and microstructure were also evaluated.

Numerous experimental heats were used to evaluate the effects of principle alloying elements. Minimum levels of chromium and molybdenum were required to obtain the desired level of corrosion resistance. Excessive chromium and molybdenum reduced corrosion resistance, hot workability, and

Table 1 Chemical Compositions of 625 PLUS, 625, and 718 Alloys

Element	Composition, wt.%: Custom Age 625 PLUS Range	Nominal	Alloy 625	Alloy 718
Carbon	0.03 max	0.01	0.04	0.04
Chromium	19.00 to 22.00	21	22	18
Molybdenum	7.00 to 9.50	8	9	3
Nickel	59.00 to 63.00	61	62	52.5
Niobium	2.75 to 4.00	3.4	3.7	5.2
Titanium	1.00 to 1.60	1.3	0.2	1.0
Aluminum	0.35 max	0.2	0.2	0.6
Iron	Bal	5	2.5	19

toughness. Extensive precipitation of chromium- and molybdenum-rich phases contributed to the reduction in properties at high chromium and/or molybdenum contents. An excellent combination of properties was obtained using 18 to 22% chromium and 7.5 to 11% molybdenum, provided the sum of the two elements did not exceed 31%.

Alloys strengthened with niobium and titanium had significantly better properties than alloys strengthened with titanium or titanium and aluminum. The best combination of properties was obtained using 2.75 to 4.25% niobium and 0.75 to 1.5% titanium. Alloys with less than about 0.75% titanium had much lower resistance to crevice corrosion than alloys with higher titanium contents. Within the ranges stated, minimum levels of niobium and titanium were required to permit age hardening to a yield strength of 827 MPa (120 ksi). On an atomic percent basis, niobium was more effective than titanium in increasing strength; consequently, compositions with more than about 1.5% titanium were not preferred. Although higher levels of niobium and titanium provided yield strengths of 965 MPa (140 ksi) and above, resistance to stress-corrosion cracking was reduced. Aluminum participates in the age-hardening reaction used to strengthen these alloys and also stabilizes the hardening precipitate. However, aluminum was a far less effective strengthener than niobium and titanium in these alloys and, for this reason, was kept below 0.35%.

In experimental alloys with yield strengths of 827 to 965 MPa (120 to 140 ksi), it was found that a nickel content of at least 60% provided good resistance to stress-corrosion cracking in boiling 45% $MgCl_2$. Low carbon contents resulted in the highest strength and best corrosion resistance and minimized precipitation of intergranular carbides during aging.

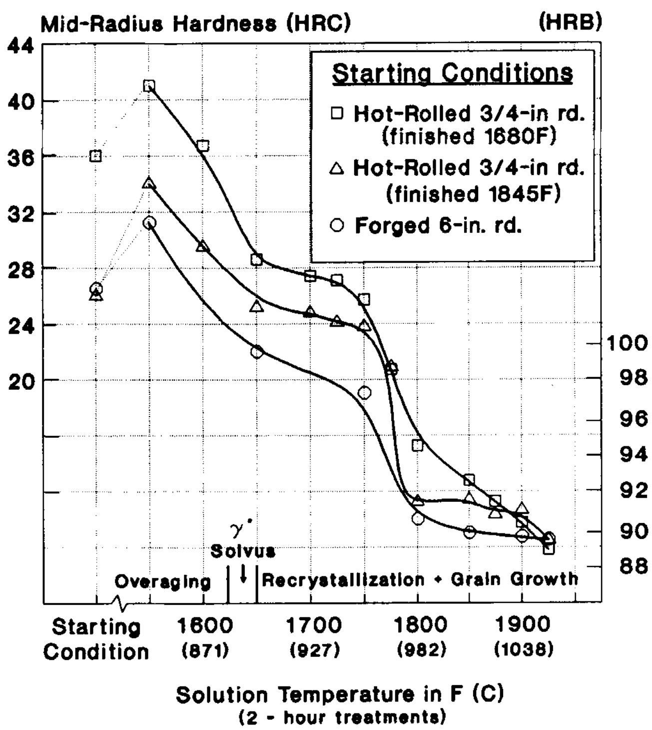

Fig. 1 Effect of solution treating temperature on hardness of 625 PLUS alloy hot finished bar.

Many of the compositions discussed above exhibited corrosion resistances similar to alloy 625 (better than alloy 718) and were age hardenable to yield strengths of 827 MPa (120 ksi) and above. Subsequent evaluations of production heats revealed that the nominal composition listed in Table 1 provided the best combination of properties. UNS NO7716 has been assigned to the alloy that is called Custom Age 625 PLUS.

3. Heat Treatment and Physical Metallurgy

Custom Age 625 PLUS alloy is solution treated and aged to obtain uniform mechanical properties and corrosion resistance in a range of product sizes. Figure 1 shows the effect of solution treatment temperature on mid-radius hardness of two 20-mm (0.78-in.) round hot rolled bars (finished at different temperatures) and a 152-mm (6-in.) round forged bar. Figure 2 shows the same effect at various locations within the cross section of a 159-mm (6.25-in.) round forged bar. A solution treatment in the range of 1024 to 1052 °C (1875 to 1925 °F) resulted in similar hardness for various products, despite differences in section size and finishing temperature. Variations in hardness within the cross section of larger forged bars were also minimized. The recrystallized grain structure is ASTM 3 or finer. Solution treatment at temperatures above about 1052 °C (1925 °F) results in coarse grain structures and lower strength. Treatment at temperatures below 982 °C (1800 °F) can result in unrecrystallized or mixed grain structures in some products.

Because of the low carbon and nitrogen contents of this alloy, few primary carbide or nitride particles (niobium/titanium-rich) are present in the as-cast condition. However, fine globular niobium/titanium-rich carbides (MC) precipitate at

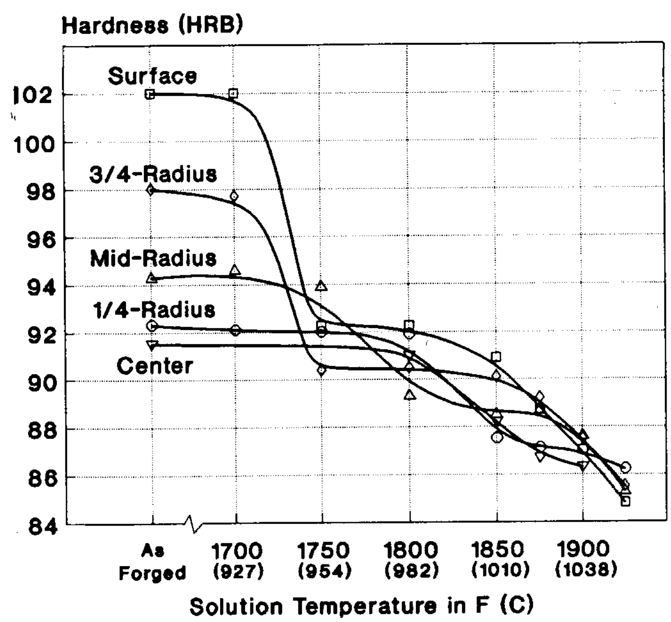

Fig. 2 Effect of solution treating temperature on hardness of 159-mm (6.25 in.) round forged bar of 625 PLUS alloy (treated 2 hr/air cooled).

temperatures of about 982 °C (1800 °F) or above. This type of precipitation is beneficial because the alloy is partially stabilized, and intergranular precipitation of undesirable chromium- and molybdenum-rich carbides ($Mc_{23}C_6$, M_6C) during a subsequent aging treatment is minimized.

Hardening elements (niobium, titanium) were balanced to provide hardness values within the 35 to 40 HRC range (approximately 120 to 140 ksi 0.2% yield strength), using a double aging treatment similar to one commonly used for alloy 718. The effects of double aging treatment times and temperatures on hardness and the extent of intergranular precipitation are shown in Fig. 3. Double aging treatments (furnace cooling between steps) resulted in a 5 to 6 HRC increase in hardness over that of the single aging treatments with little or no additional intergranular precipitation. The double 8-hr cycle provided slightly higher hardness compared to the double 4- or 2-hr cycles. Underaging during the primary aging treatment minimized intergranular carbide precipitation. A double aging treatment of 732 °C (1350 °F) for 8 hr, furnace cool 55 °C/hr (100 °F/hr) to 621 °C (1150 °F), 8 hr, air cool resulted in the highest hardness with minimal intergranular precipitation. Strengthening occurs via precipitation of a very fine γ'' phase (Ni_3/Nb, Ti, Al) during aging. The microstructure of Custom Age 625 PLUS in the solution annealed plus aged (1350 °F + 1150 °F) condition is shown in Fig. 4.

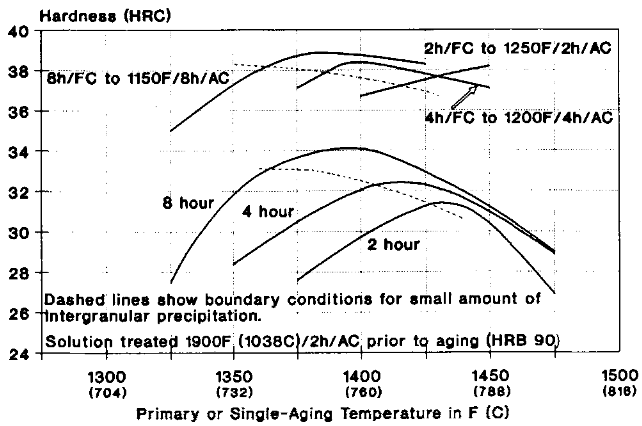

Fig. 3 Effect of single and double aging treatments on hardness of solution treated ¾-in.^{2} bar of 625 PLUS alloy.

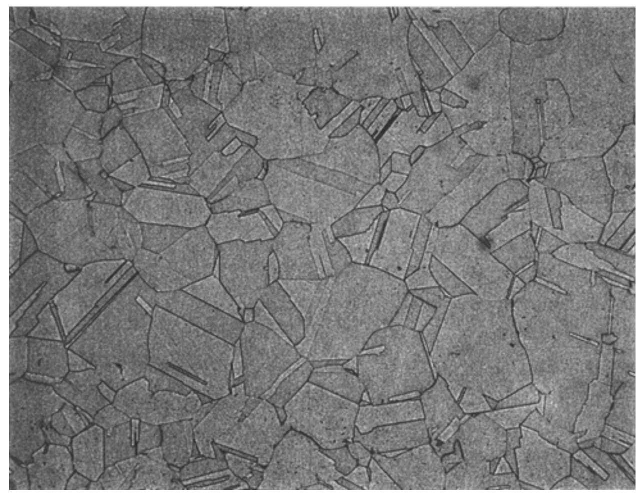

Fig. 4 Microstructure in the solution annealed plus aged condition. 100×.

Table 2 Typical Room-Temperature Tensile Properties of 625 PLUS, 625, and 718 Alloys

Alloy	Size, mm	Size, in.	Aging treatment	Yield strength, 0.2%, MPa	Yield strength, 0.2%, ksi	Ultimate tensile strength, MPa	Ultimate tensile strength, ksi	Elongation in 4*D*, %	Reduction in area, %
Alloy 625 PLUS, round........	152	6	730 °C, 8 hr, FC to 620 °C, 8 hr, AC	917	133	1262	183	32	53
Alloy 625, round..................	152	6	640 °C, 64 hr, AC	552	80	972	141	46	58
	57	2.25	650 °C, 74 hr, AC	869	126	1186	172	31	37
Alloy 625, plate....................	13	0.5	Cold rolled 25%, no aging	889	129	1048	152	29	59
Alloy 718, round..................	152	6	788 °C, 8 hr, AC	910	132	1227	178	26	33
	127	5	720 °C, 8 hr, FC to 620 °C, 8 hr, AC	1200	174	1400	203	16	30

Table 3 Effects of Specimen Location and Orientation on Room-Temperature Mechanical Properties

Alloy	Specimen orientation	Test location	Yield strength, 0.2%, MPa	Yield strength, 0.2%, ksi	Ultimate tensile strength, MPa	Ultimate tensile strength, ksi	Elongation in 4*D*, %	Reduction in area, %	Charpy V-Notch impact energy, J	Charpy V-Notch impact energy, ft · lb
Alloy 625 PLUS, aged.......	L	Center	869	126	1241	180	35	52	102	75
	L	Midradius	889	129	1262	183	33	56	100	74
	T	Midradius	883	128	1234	179	31	54	92	68
	L	Surface	958	139	1310	190	31	55	94	69
Alloy 625, cold rolled........	L	...	910	132	1062	154	27	61	119	88
	T	...	876	127	1020	148	24	47	62	46
Alloy 718, aged.................	L	Midradius	979	142	1269	184	28	48	79	58
	T	Midradius	972	141	1262	183	25	39	43	32

Table 4 Room-Temperature Tensile Properties of Various Bar Sizes of 625 PLUS Alloy

Bar size mm	Bar size in.	No. of bars	No. of tests	Yield strength, 0.2% MPa	Yield strength, 0.2% ksi	Ultimate tensile strength MPa	Ultimate tensile strength ksi	Elongation in 4D, %	Reduction in area, %
184	7.25	1	6	910	132	1276	185	32	51
152	6.00	13	25	917	133	1262	183	32	53
127	5.00	2	4	931	135	1262	183	32	53
102	4.00	2	4	924	134	1282	186	33	54
70	2.75	1	1	862	125	1250	181	35	53
38	1.50	3	5	896	130	1282	186	31	56
25	1.00	3	3	917	133	1310	190	33	55

Table 5 Autoclave Stress-Corrosion Cracking Test Results

Alloy	Size mm	Size in.	Condition	Yield strength, 0.2% MPa	Yield strength, 0.2% ksi	No. cracked/ No. tested C-rings	No. cracked/ No. tested U-bends
Alloy 625 PLUS, round	159	6.25	1040 °C, 2 hr, AC + 718 °C, 8 hr, FC to 621 °C, 8 hr, AC	834	121	...	0/2
			1040 °C, 2 hr, AC + 732 °C, 8 hr, FC to 621 °C, 8 hr, AC	896	130	0/2	0/2
			1040 °C, 2 hr, AC + 746 °C, 8 hr, FC to 621 °C, 8 hr, AC	958	139	0/2	0/2
Alloy 625, plate	4.6	0.18	Cold rolled 24 to 25%	827	120	...	1/6
				869	126	0/1	...
	8.2	0.32	Cold rolled 32%	972	141	...	0/2
Alloy 718, round	152	6.0	1025 °C, 2 hr, WQ + 788 °C, 8 hr, AC	910	132	1/2	2/2

Note: The environment consisted of 25% NaCl + 0.5 g/l S + 9.7 MPa (1400 psig) H_2S at 204 °C (400 °F) for 28 days (672 hr).

Although the nickel and niobium contents of 625 and 625 PLUS alloys are similar, the higher titanium content of 625 PLUS greatly accelerates the aging response. Thus, yield strengths of 827 MPa (120 ksi) or above can be obtained by aging for 24 hr or less, whereas much longer aging times (>70 hr) would be required to obtain similar strength levels in annealed alloy 625.

4. Mechanical Properties

Table 2 contains typical room-temperature tensile properties for 625 PLUS, 625, and 718 alloys. Alloy 625 cannot be hardened to obtain yield strengths above 827 MPa (120 ksi) without cold working or using very long aging treatments. Warm working combined with long aging times has been used to strengthen smaller section sizes of alloy 625 to yield strengths above 827 MPa (120 ksi), but warm or cold working becomes less practical as section size increases.[5] Yield strengths of 827 to 965 MPa (120 to 140 ksi) can be obtained in 625 PLUS alloy using an 18-hr double aging treatment similar to that used for aerospace alloy 718. Because strengthening of 625 PLUS does not depend on warm or cold working, a full solution treatment is used to obtain the optimum uniformity. Similar strength levels are obtained in alloy 718 by overaging at about 788 °C (1450 °F), following solution treatment at 1025 °C (1875 °F).[6] Although other modifications of Alloy 625 with higher niobium contents or the addition of titanium has been reported in technical papers, limited data compilations of properties have been released.

Table 3 shows the effects of specimen orientation and location on room-temperature tensile and Charpy V-notch impact properties of 625 PLUS, 625, and 718 alloys. Yield strengths of 827 to 965 MPa (120 to 140 ksi), along with high ductility and toughness, were obtained for 625 PLUS alloy at various locations throughout a 152-mm (6-in.) round bar. Solution-treated and aged 625 PLUS alloy had similar tensile properties and impact energies in the longitudinal and transverse orientations, whereas cold worked alloy 625 and aged alloy 718 had lower properties in the transverse orientation. Table 4 shows that room-temperature tensile properties of heat treated 625 PLUS bar, ranging in diameter from 25 to 184 mm (1.00 to 7.25 in.), were similar, which indicates that strengthening is not dependent on section size.

5. Corrosion Resistance

5.1 *Stress-Corrosion Cracking Resistance*

Autoclave environments containing elemental sulfur and high-pressure H_2S in saturated brine at 204 °C (400 °F) were used to simulate severe conditions expected in some deep sour-gas wells. Stress-corrosion cracking results for C-ring and U-

Table 6 Effect of Aging Treatment on Sulfide-Stress-Corrosion Cracking

Aging treatment	Yield Strength, 0.2% MPa	ksi	Hardness HRC	Tensile	U-bend	DCB
718 °C, 8 hr, FC to 621 °C, 8 hr, AC	827	120	35 to 36	...	NC, NC	NC, NC
732 °C, 8 hr, FC to 621 °C, 8 hr, AC	896	130	38	NC	NC, NC	NC, NC
746 °C, 8 hr, FC to 621 °C, 8 hr, AC	958	139	39 to 40	NC	NC, NC	NC

Note: Tests were conducted on 159-mm (6.25-in.) round bars in 5% NaCl + 0.5% acetic acid + H_2S (NACE TM0177) at 24 °C (75 °F).

Table 7 Pitting Temperature Test Results for 625 PLUS, 625, and 718 Alloys

Alloy	Size mm	in.	Condition	Pitting temperature, °C, in: 6 wt.% $FeCl_3$ + 1 wt.% HCl(a)	Modified green death solution (b)
Alloy 625 PLUS, round	159	6.25	1040 °C, 2 hr, AC + 732 °C, 8 hr, FC to 621 °C, 8 hr, AC	>98, >98	75, 80
Alloy 625, plate	4.6	0.18	Cold rolled 24 to 25%	>98, >98	80, 90
Alloy 718, round	152	6.0	1025 °C, 2 hr, WQ + 788 °C, 8 hr, AC	56, 62	45, 45

(**a**) 24-hr exposure. Temperature was increased in 2.5 °C intervals, with no preparation of specimens between exposures. (**b**) 96-hr exposure. Modified green death solution consists of 7 vol.% H_2SO_4 + 3 vol.% HCl + 5 wt.% $CuCl_2 \cdot 2H_2O$ + 5 wt.% $FeCl_3 \cdot 6H_2O$. Temperature was increased in 5 °C intervals and specimens were ground between exposures.

Table 8 Crevice Corrosion Test Results for 625 PLUS, 625, and 718 Alloys

Alloy	Size mm	in.	Condition	Weight loss, mg/cm^2, in 6 wt.% $FeCl_3$ + 1 wt.% HCl 40 °C	55 °C	Crevice temperature, °C, in in yellow death solution(a) after 96 hr
Alloy 625 PLUS, round	159	6.25	1040 °C, 2 hr, AC + 732 °C, 8 hr, FC to 621 °C, 8 hr, AC	1.2	6.0	40, 40
Alloy 625, plate	4.6	0.18	Cold rolled 24 to 25%	3.7	13.7	35, 40
Alloy 718, round	152	6.0	1025 °C, 2 hr, WQ + 788 °C, 8 hr, AC	35.0	47.2	<25, <25

(**a**) Yellow death solution consists of 4 wt.% NaCl + 0.1 wt.% $Fe_2(So_4)_3$ + 0.01*M* HCl. Temperature was increased in 5 °C intervals and specimens wet ground between exposure.

bend samples of age-hardened 625 PLUS and 718 alloys and cold worked 625 are listed in Table 5. Samples of 625 PLUS alloy with yield strengths up to 958 MPa (139 ksi) resisted cracking at 204 °C (400 °F) for 28 days. For comparison, one of the nine alloy 625 samples cracked and three of the four alloy 718 samples cracked.

Steel-coupled tensile, U-bend, and double-cantilever beam (DCB) specimens were treated in the NACE TM0177 environment (5% NaCl + 0.5% acetic acid purged with H_2S) to evaluate resistance to sulfide-stress-cracking/hydrogen embrittlement at ambient temperature. Results in Table 6 show that transverse tensile (stressed at 100% of 0.2% yield strength) and U-bend specimens of 625 PLUS alloy resisted cracking at yield strength levels of 827 to 958 MPa (120 to 139 ksi). No crack growth was observed in any of the fatigue precracked DCB samples with final stress intensities of 58 to 75 MPa$\sqrt{m}$ (53 to 68 ksi$\sqrt{in.}$). Based on the excellent stress-cracking resistance demonstrated in ambient temperature and 204 °C (400 °F) tests, 625 PLUS alloy in the solution treated and aged condition (HRC 40 maximum hardness) has been included in the NACE MR0175 document.

5.2 *Pitting and Crevice Corrosion Resistance*

Pitting and crevice corrosion tests were performed in several chloride-containing solutions, as shown in Tables 7 and 8. The modified green death solution is a simulated service environment, whereas the yellow death solution has been useful in ranking the pitting resistance of a wide range of alloys. 625 PLUS alloy displayed pitting and crevice corrosion resistance similar to alloy 625 and superior to alloy 718.

6. Summary

Custom Age 625 PLUS is a nickel-base alloy strengthened by precipitation of γ'' [Ni_3(Nb, Ti, Al)] during aging. Large section sizes can be age hardened to yield strengths (0.2%) above 827 MPa (120 ksi) without cold or warm working. Excellent ductility and toughness are retained following age hardening. Solution treatment before aging results in uniform properties and microstructures for a variety of product sizes, as well as throughout the cross sections of larger diameter bars.

The chemical composition of 625 PLUS alloy was optimized to provide corrosion resistance similar to that of cold worked alloy 625 and superior to that of age-hardened alloy 718 in many environments. The alloy is highly resistant to pitting and crevice corrosion by chlorides, sulfide-stress-cracking in the NACE TM0177 environment, and stress-corrosion cracking in environments containing brine, hydrogen sulfide, and elemental sulfur at high pressures and temperatures. Because of its high strength and resistance to corrosive environments, 625 PLUS alloy is being used in oil field and marine applications.

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