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New spans to reconnect Louisiana highway



A fiber optic sensor is bonded to a tailings pipe in a serpentine configuration. The sensor, made of coil and grid mesh and weighing as little as 2 oz (28 g), is designed to measure temperature, pressure, and the subtle, localized swelling of pipeline walls that signals the presence of corrosion (p. 14). Photo courtesy of FOX-TEK.

An article beginning on p. 44 describes the results of an investigation into the premature water-side corrosion of furnace wall tubes of a high-pressure boiler. This is a typical photomicrograph of the water-side scales showing a discontinuous, inner magnetite layer. Original magnification 200X.



UNS N06625: A Current Review of the Literature

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The mechanical and electrochemical characteristics of nickel-based alloys have been extensively examined for their potential application in high- and elevated-temperature and marine environments. This article presents a literature review concerning the behavior of alloy UNS N06625 and other nickel-based alloys in these environments.

All nickel-based alloys have an austenitic face-centered-cubic microstructure. The specified compositional limits for alloy 625[†] (UNS N06625), a single-phase Ni-Cr-Mo alloy, are provided in Table 1. The corrosion resistance of this alloy has been attributed to the synergistic effect of chromium and molybdenum (Tables 2 and 3).¹⁻³ The following review is a concise examination of applications of wrought and clad UNS N06625.

The wrought alloy was not susceptible to localized corrosion in environments typical of sour gas wells (i.e., 0.21 MPa hydrogen sulfide [H₂S] and 0.70 MPa carbon dioxide [CO₂] with 50 and 30,000 ppm chlorides).⁴ The alloy clad to AISI 4130 (UNS G41300) low-alloy steel exhibited the same corrosion resistance as the wrought alloy in environments char-

[†]Trade name.

acteristic of deep sour oil and gas wells (i.e., temperatures of 204 to 260°C and pressures of 138 MPa [20,000 psi] in the presence of H₂S and chlorides).⁵⁻⁶ The clad material resisted sulfide stress cracking at stresses of 120% yield strength and chloride stress corrosion cracking at stresses of 100% yield strength. Test panels of the alloy clad steel resisted corrosion in wet flue gas scrubber systems.⁷ Hibner and Morse⁸ demonstrated the corrosion resistance of the alloy clad steel with weld material (12% Mo) in sulfur dioxide (SO₂) scrubbers. Rogne,⁹ however, demonstrated that the alloy weld overlays on 6 Mo stainless steel (SS) did not improve resistance to crevice corrosion.

Oldfield and Sutton¹⁰⁻¹¹ used mathematical modeling to define a critical crevice solution (CCS) in terms of pH and Cl⁻ required to produce an anodic current density of at least 10 µA/cm² (i.e., a penetration rate for SS of 0.1 mm/y). They determined that for UNS N06625, the CCS required a pH from -0.25 to 0.50 and 6M Cl⁻. McCafferty, et al.¹² demonstrated that active crevices contained concentrated amounts of dissolved Ni²⁺, Cr³⁺, Mo³⁺, and Fe²⁺, in addition to low pH and Cl⁻. Using model crevice electrolytes containing dissolved metal cations, they were able to demonstrate crevice corrosion in UNS N06625 in natural seawater at 25°C.

The Oldfield-Sutton¹⁰⁻¹¹ model for crevice corrosion in this alloy required a large crevice depth/gap ratio to decrease

TABLE 1
COMPOSITION OF
UNS N06625 ALLOY

Element	Range—Limit (%)
Al	0.40 max.
C	0.10 max.
Nb	3.15 – 4.15
Cr	20.0 – 23.0
Fe	0.50 max.
Mn	0.50 max.
Mo	8.0 – 10.0
Ni	Remainder
P	0.015 max.
S	0.015 max.
Si	0.50 max.
Ti	0.40 max.

diffusivity/convection and promote the development of CCS, providing a sufficient electrolyte path length to exceed the voltage drop required for crevice initiation.¹³ Oldfield, et al.¹⁴ predicted that the crevice gap required for the development of CCS in this alloy was <0.1 μm (Figure 1). The most commonly encountered gaps are between 0.2 and 0.5 μm . Watson and Postlethwaite¹⁵ developed a mathematical model for calculating the incubation time for crevice corrosion that included all metal and metal hydroxide species in the CCS. Their model accurately predicted incubation times for type 304 SS (UNS S30400) and type 316L SS (UNS S31603), but not UNS N06625.

High- and Elevated-Temperature Environments

Wrought¹⁶ and composite¹⁷ alloys have been used in commercial incinerators for industrial and municipal wastes containing mixed oxidants combined with carbon, sulfur, and halide vapors at 593 to 927°C. The alloy has been evaluated in the following aqueous solutions typical of supercritical water oxidation processes: hydrochloric acid (HCl)/oxygen¹⁸⁻¹⁹ and sulfuric acid (H₂SO₄)/oxygen under supercritical (temperature >374°C and pressure >22.1 MPa) and subcritical conditions;¹⁹⁻²⁰ chloride/oxygen in high subcritical temperatures;²¹ sulfate solutions at high temperature (up to 500°C) and high pressure (38 MPa),²² and others.²³ In aqueous solutions containing up to 0.2 mol/kg H₂SO₄ and up to 1.44 mol/kg oxygen at 24 MPa, no corrosion was observed below 150°C. Between 150 and 200°C, some intergranular attack was observed and at 250°C, shallow pits formed as a result of transpassive corrosion. The upper temperature limit for severe corrosion of the alloy was 390°C.²⁰ Under laboratory conditions, the alloy corroded in oxidizing HCl solutions at 350°C and 24 MPa after 0.75 to 50 h. Pits grew faster on polished surfaces.¹⁹ Corrosion was reduced when stable oxides were allowed to form prior to exposure. In summary, alloy UNS N06625 is fre-

TABLE 2
POSSIBILITY OF CREVICE CORROSION INITIATION AND MAXIMUM DEPTH OF ATTACK OF VARIOUS SS EXPOSED FOR 30 DAYS TO SEAWATER AT 15°C. MULTICREVICE ASSEMBLY—120 CREVICES PER STEEL

SS	Probability of Crevice Corrosion Initiation %	Maximum Depth of Attack (mm)
17% Cr (430)	52	1.17
18% Cr 10% Ni (304)	13	0.28
18% Cr 10% Ni 2-2.5% Mo (316)	2	0.03
18% Cr 12% Ni 3-3.5% Mo (317)	0	0

Reproduced from Todd² with permission from the Nickel Institute.

TABLE 3
CREVICE CORROSION OF NICKEL-BASED ALLOYS (MCA TESTS 120 CREVICE SITES)

Material	No. of Sites Attacked	Depth of Attack (mm)
UNS N08825 (2.7% Mo)	37	0.25-2.42
UNS N06007 (5.8% Mo)	6	0.02-0.87
UNS N06625 (8.5% Mo)	0	0
UNS S66286 (15.5% Mo)	0	0

Reproduced from Todd² with permission from the Nickel Institute.

quently used as reactor material for supercritical water oxidation applications, with the notable exceptions of the preheater and cooler parts of the reactor.²⁴

The alloy was a candidate material for high-level nuclear waste storage in underground repositories.²⁵⁻²⁶ Kehler, et al.²⁷ studied crevice corrosion of the alloy at temperatures ranging from 60 to 95°C in concentrated chloride electrolytes, simulating conditions expected to evolve from episodic evaporation and rewetting on the waste canister. It was concluded that crevice corrosion stabilization was influenced by electrolyte compositions, but not pH. Crevice stabilization occurred at more active potentials in electrolytes with chloride: total oxyanions ratios of 100:1, as compared to 10:1. Repassivation potentials were not influenced by electrolyte composition, pH, or accumulated anodic charge. Kehler, et al.²⁸⁻²⁹ also concluded that there were two potential mechanisms for corrosion failure in a proposed repository: transpassive dissolution of the protective oxide under highly oxidizing conditions at elevated pH and crevice cor-

rosion, depending on the electrolyte, temperature, and oxide age.

Martin, et al.³⁰ studied the crevice susceptibility of the alloy in elevated-temperature (65°C) natural seawater. They demonstrated that crevice corrosion initiation and propagation were influenced by electrochemical potential and that crevice corrosion could initiate in a matter of hours at +300 mV (silver/silver chloride [Ag/AgCl]). Martin, et al.³¹⁻³² established a critical potential-temperature-time relationship needed to initiate crevice corrosion in the alloy. The potential required to initiate crevice corrosion decreased (became less noble) when the temperature was increased from ambient to 40°C. The crevice initiation potential decreased from 300 mV (Ag/AgCl) for ambient seawater to 100 mV (Ag/AgCl) for 40°C. The time required to initiate crevice corrosion decreased as the temperature increased. Martin, et al.³³ compared the crevice corrosion resistance of five Ni-Cr-Mo alloys in seawater (ambient to 65°C). All alloys were susceptible to crevice corrosion in elevated-temperature seawater (Table 4).

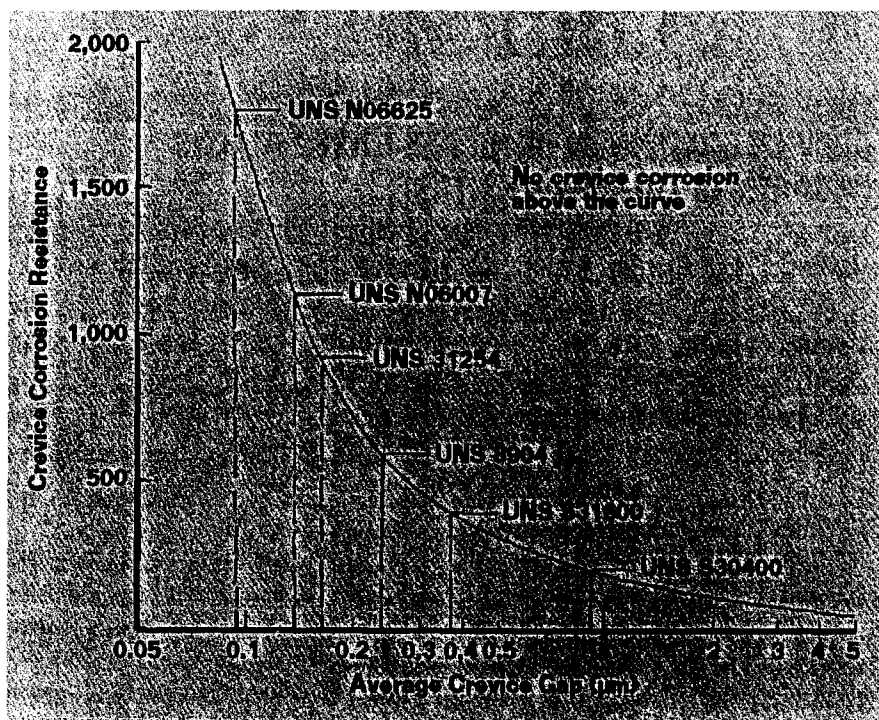
TABLE 4

SUSCEPTIBILITY OF VARIOUS SS TO CREVICE CORROSION IN SEAWATER AT ELEVATED TEMPERATURES

Material	t_{INIT} at 65°C/ 300 mV (h)	d_{CREV} at 65°C/ 300 mV	Crevice Morphology
UNS N06625	2.9	0.5 mm/d	Furrowed
UNS N06022	9.5	0.08 mm/d	Pitted
UNS N06059	16	0.02 mm/d	Furrowed
UNS N06200	20	0.04 mm/d	Pitted
UNS N06686	>120	Isolated etch	Furrowed (at 550 mV)

Reproduced from Martin, et al.³³ Copyright NACE International, 2004.

FIGURE 1



Crevice corrosion model prediction of required gap size for the development of CCS of various SS and nickel-based alloys. Adapted from Oldfield, et al.¹⁴

Marine Environments

The Nickel Development Institute³⁴ tabulated data from Hack,³⁵ demonstrating the crevice corrosion resistance of UNS N06625 in seawater exposures (Table 5). Klein, et al.³⁶ demonstrated that highly chlorinated seawater (85 to 90 mg/L) produced rapid crevice corrosion initiation within 24 h and extensive propagation. The maximum depth of attack after 60 h was 2.3 μm . The alloy was susceptible to crevice attack in natural and chlorinated seawater (1 mg/L) and

the magnitude of attack was similar in both waters. They observed that propagation increased with velocity, that the composition of the crevice former had no effect on susceptibility, and that crevice geometry had a significant effect on rate. Lillard and Scully¹³ modeled crevice corrosion of the alloy in chlorinated and nonchlorinated ASTM artificial seawater. Model results were in agreement with remote crevice assembly experiments, showing that crevice corrosion occurred more readily in the chlorinated artificial seawater.

Al-Odwani, et al.³⁷ conducted crevice corrosion tests using a multiple crevice washer assembly with flowing seawater and neutral brine (flow rates of 100 L/h for 3,000 and 6,000 h) at 30°C. Exposure conditions were typical of reverse osmosis plants. Crevices were observed in UNS N06625. The severity of crevice corrosion for nickel alloys decreased as the percentage of molybdenum increased. Martin, et al.³³ demonstrated dramatically different crevice corrosion initiation behavior among Ni-Cr-Mo alloys when using apparently comparable fluorelastomeric gasket materials. Differences were attributed to corrosion-inhibiting properties of mold release compounds in some gasket materials.

Inman, et al.³⁸ determined the initiation time and propagation rate associated with UNS N06625 in natural seawater using polarization measurements. Vinyl sleeves were used to create crevices. They observed that the affected area of crevice corrosion increased continually following initiation, while the depth of attack remained relatively constant and shallow. In their tests, crevice corrosion initiated in UNS N06625 samples faster than in UNS S31600 samples. Mass loss from the UNS S31600 samples was approximately double that of UNS N06625.

Neville and Hodgekiess³⁹ examined passive films on SS and nickel alloys before and after exposure to synthetic seawater. Higher Fe/Cr ratios are typically indicative of lower corrosion resistance. However, they found that the Fe/Cr ratios for SS and nickel alloys were not directly proportional to the measured ratios in the bulk alloy. The Fe/Cr ratio invariably increased after exposure to seawater for 5 h. Mo could be detected only in the passive

TABLE 5

CREVICE CORROSION RESISTANCE OF VARIOUS SS IN SEAWATER

UNS	Chemical Composition wt% (Nominal)					No. of Sites Attacked		No. of Sides Attacked	Depth of Attack (mm)	Initiation Time (h)
	Cr	Ni	Mo	Mn	Cu	Per Side	Total			
S31600	17.5	10.7	2.4	1.6	0.3	1-13	33	6	0.29-1.93	24-102
S21600	20	6	2.5	8	—	7-10	50	6	0.10-0.64	51-77
S31675	21.3	9.4	2.7	3.8	—	2-9	39	6	0.01-1.00	51
S31703	18.9	12.2	3.6	1.7	—	7-20	91	6 ^(A)	0.18-1.92	51-77
S31725	19.5	14.5	4.1	1.3	0.2	19-20	116	6	0.01-1.07	51-77
S20910	21.1	13.7	2.3	4.8	—	16-20	112	6	0.10-1.10	36-77
N08904	20.5	24.7	4.7	1.5	1.6	0-13	36	5	0.14-0.74	51-365
S31254	20.0	17.9	6.1	0.5	0.8	0-7	18	5	0.02-0.51	51-479
N08366	20.4	24.6	6.4	1.4	—	0-3	11	4	0.01-0.62	51-365
N08320	21.6	25.5	5.0	0.9	—	0-5	6	2	0.12-0.46	51-365
N08020	19.4	33.2	2.2	0.4	3.2	0-15	49	5	0.14-3.10	51-171
N08026	23.9	33.4	5.6	0.4	3.3	0-6	13	3	<0.01-0.53	365-507
N08825	22.0	44.0	2.7	0.4	1.7	413	37	6 ^(A)	0.25-2.42	51-221
N06007	22.2	46.8	5.8	1.5	1.8	0-2	6	4	0.02-0.87	365-673 ^(C)
N06985	22.8	43.7	7.0	0.8	1.8	0-2	2	1	0.06-0.21	102
N06625	22.3	61.0	8.5	0.1	—	0	0	0	—	—
S66286	15.5	54.7	15.5	0.5	0.1	0	0	0	—	—
J92900	19.3	10.0	2.4	1.0	—	4-17	74	6	0.16-3.77	126 ^(C)
J95150	20.0	28.2	2.5	0.2	3.1	13-18	99	6 ^{(B),(D)}	0.15-2.33	126 ^(C)
S32550	25.2	5.2	2.5	1.0	3.2	0-14	37	4 ^(B)	0.03-2.21	126-169

^(A)Gravity-assisted tunneling.

^(B)Some attack initiating outside of crevice area.

^(C)Initiation not observed on some panels where attack occurred.

layer of alloys containing more than 4% Mo. No Ni was detected in any of the passive films. Neville and Hodgekiess³⁹ determined that the breakdown potential for UNS N06625 was ~ +800 mV (vs saturated calomel electrode).

The impact of marine microfouling and macrofouling on the crevice corrosion of UNS N06625 has been studied to a limited extent. Kain⁴⁰ exposed test panels (10 by 15 cm) for one year at Wrightsville Beach, North Carolina. Observations included hard fouling (barnacles) on the panels, but no evidence of crevice corrosion. Neville and Hodgekiess⁴¹ exposed the alloy long-term in natural seawater off the coast of Scotland. After 18 months, all materials were heavily fouled with barnacles and mussels, and all materials exhibited crevice corrosion. Martin, et al.³⁰ found that ennoblement from biofilm formation produced corrosion potentials that exceeded the crevice corrosion initiation potential in ambient seawater. Enos and Taylor⁴² demonstrated that UNS N06625 was resistant to attack by sulfate-reducing bacteria. The possibility that biofilms or colonies of bacteria could

cause crevice corrosion of this alloy has never been investigated.

In addition to crevice corrosion, two mechanisms have been identified as causing corrosion failures in this alloy in seawater service. Rogers⁴³ evaluated the failure of UNS K31820 (HY-80)/UNS N06625 studs used to secure external equipment to the hull of a ship. Cracking at the weld region was attributed to environmentally assisted cracking. Other stud failures were attributed to corrosion of the UNS K31820 portion of the stud where the protective coating failed, permitting galvanic interactions. Harris and Clatworthy⁴⁴ showed that cathodic charging of tensile specimens undergoing slow strain extension did not produce hydrogen embrittlement (HE) of UNS N06625. Pulling tensiles of previously charged specimens did produce HE in this alloy.

UNS N06625 is sometimes considered for the replacement of 70/30 Cu/Ni in seawater piping systems, creating the possibility for galvanic corrosion between the dissimilar metals.⁴⁵ Hack and Wheatfall⁴⁵ measured galvanic currents between this alloy and 70/30 couples that started high

and decayed with time. They found that typical rubber insert isolation couplings did not provide effective electrical isolation because of possible alternative electrical shorting paths, such as pipe hangers, electrical safety grounding straps, electrically actuated pumps and valves, electrical grounds, metal braid hydraulic lines, metal ladders, tools, and metal cleaning pads. They described 1- to 3-m separators to reduce the possibility of galvanic corrosion. The separators were most effective under low-flow conditions where the possibility for galvanic corrosion was greatest. Stray current-induced crevice corrosion was described as the primary corrosion mode for UNS N06625 separators.

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BRENDA J. LITTLE, FNACE, is a senior scientist at the Naval Research Laboratory. She uses surface analytical chemistry, electron microscopy, and electrochemical techniques to investigate adsorption, biofouling, biodegradation, bioremediation, and corrosion in marine environments. She is a NACE Fellow and has been a NACE member since 1984. **MP**