Stress-Rupture Behavior of Waspaloy and IN-738LC at 600°C (1112°F) in Low Oxygen Gaseous Environments Containing Sulfur

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Abstract

Stress-rupture lives of precipitation strengthened Nickel base Superalloys are detrimentally effected when subjected to atmospheres consisting of a low oxygen partial pressure and a high sulfur partial pressure. Short time failures, originating at mechanical notches, in these atmospheres have been experienced under both service and laboratory conditions. This notch sensitive behavior has previously been documented.[1,2] During laboratory testing of various specimens, trends have emerged to suggest that grain size can influence notch behavior in corrosive gaseous environments.

Introduction

Fluidized Catalytic Cracker Units (FCCU) are used by refineries to convert crude oil into lighter hydrocarbons such as propane, kerosene, gasoline, and fuel oil. During this process a catalyst is used to strip away some of the carbon atoms from the crude. The spent catalyst is heated in a regenerator to burn-off the carbon, and then the rejuvenated catalyst is returned to the reactor to repeat the cycle again. Exhaust gasses from the regenerator are directed through a FCCU Expander, i.e. a power turbine in the exhaust flue, to reclaim waste energy.

Regenerator atmospheres at refineries are divided into two groups, complete combustion and partial combustion. Thermodynamically calculated equilibrium diagrams can be used to compare these two atmospheres (Fig. 1). It can be seen that while the complete combustion process contains sufficient oxygen to predict the formation of protective chromium oxide and nickel oxide scales, the partial combustion process contains less oxygen, and therefore would be expected to produce chromium oxide and nickel sulfide scales.

Expanders powered by partial combustion atmospheres have become increasingly susceptible to failure as the sulfur content of available crude oils is increasing and the demand for higher horsepower continues. Service failures of FCCU Expanders in this atmosphere have revealed very similar metallurgical features. In all but one case, fracture had originated from a blade or disc firtree serration and progressed by intergranular separation. When the fractures / cracks were viewed in cross-section, a two layered scale was present. The scale immediately adjacent to the base metal had a gray colored appearance and consisted primarily of chromium, oxygen, and sulfur. The scale along the crack centerline had a gold colored appearance and consisted primarily of nickel and sulfur.

These sulfidation fractures are notably different from low temperature type II (layer-type) hot corrosion. Fractures resulting from this mechanism: exhibit an intergranular topography, occur below the 635°C (1175°F) nickel sulfide eutectic temperature, and contain no salts in the scales. It has been evident since the first occurrence in the early 1980s, that this sulfidation fracture mode was due to the combined effects of stress, temperature, time, and a low oxygen atmosphere containing sulfur.

A paper published by Mr. Ken Natesan, of Argonne National Laboratory, entitled "Effect of Oxidation / Sulfidation on Creep Behavior of Alloy 800" revealed similar two layered scales in the test range of 650°C to 927°C.[3] For Alloy 800, the scales were identified as iron sulfide and either chromium oxide or chromium sulfide depending upon test atmosphere. Mr. Natesan concluded that the alloy suffered substantial reductions in creep life when the test environment pO_2 was less than the transition boundary pO_2 between chromium oxide / chromium sulfide formation.

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Temperature, Equipment, & Procedure

The test temperature of 600°C (1112°F) was selected to promote stress-rupture failure of Waspaloy in air, and stay below the 635°C (1175°F) nickel sulfide eutectic temperature. A direct comparison between stress-rupture results in air and the corrosive atmosphere was desired.

Laboratory testing was performed using mixed gases of hydrogen and hydrogen sulfide slowly bubbled through distilled water to produce the desired atmospheres. Atmosphere 1 was achieved by bubbling a 51.3 % H_2S – 48.7 % H_2 mole percent mixture through room temperature water. Atmosphere 2, 3, or 4 was produced by bubbling a 5.9 % H_2S – 94.1 % H_2 mole percent mixture through room temperature, 45°C, or 80°C water. At the test temperature of 600°C, these atmospheres were (Fig.1):

Atmosphere 1:	Log O_2 = - 26.3	Log S_2 = - 5.6
Atmosphere 2:	Log O_2 = - 26.9	Log S_2 = - 8.0
Atmosphere 3:	Log O_2 = - 25.9	Log S_2 = - 8.0
Atmosphere 4:	Log O_2 = - 24.0	Log S_2 = - 8.1

Equipment used for the tests consisted of a stress-rupture frame, pressurized cylinders of mixed gases, distilled water, and a stainless steel reaction chamber. Connection of the gas system was accomplished by a 304 stainless steel supply tube from the flow meters on the pressurized cylinders to the bottom of the pot of water. Another 304 stainless steel supply tube extended from the top of the water pot to the lower end plate of the reaction chamber. Variac heating tape was used to prevent the condensation of water vapor in the later supply tube. The reaction chamber was 304 stainless steel schedule 40 pipe approximately 48 cm long x 5.3 cm inside diameter (19 inches long x 2.1 inches ID) with flanges welded on both ends, and end plates bolted to the flanges. Thermo-well tubes of 304 stainless steel entered the reaction chamber just above and below the specimen shoulders, approximately 90 mm (3.6 inches) apart. Temperature control was maintained by a thermo-couple placed in the upper thermo-well. Specimen gauge temperatures of 600+/-2°C (1112+/-4°F) were recorded during equipment calibration.

The stress-rupture frame was of a standard Satec design, incorporating a 20:1 specimen load to pan weight ratio. Furnace around the reaction vessel was of a clam shell design operated by a single zone controller.

A sixteen hour nitrogen gas purge was used to vent oxygen from the system prior to each test. The furnace was turned on, and the corrosive gas mixture was flowed at 0.1 SCFM. After about four hours, the temperature of the upper thermo-well indicated the specimen had achieved 600°C (1112°F). Test temperature was stabilized for 10 minutes prior to applying load.

Alloys Tested

Waspaloy received the greatest amount of testing during this project. Other forging alloys tested were X-750 and U-720Li.

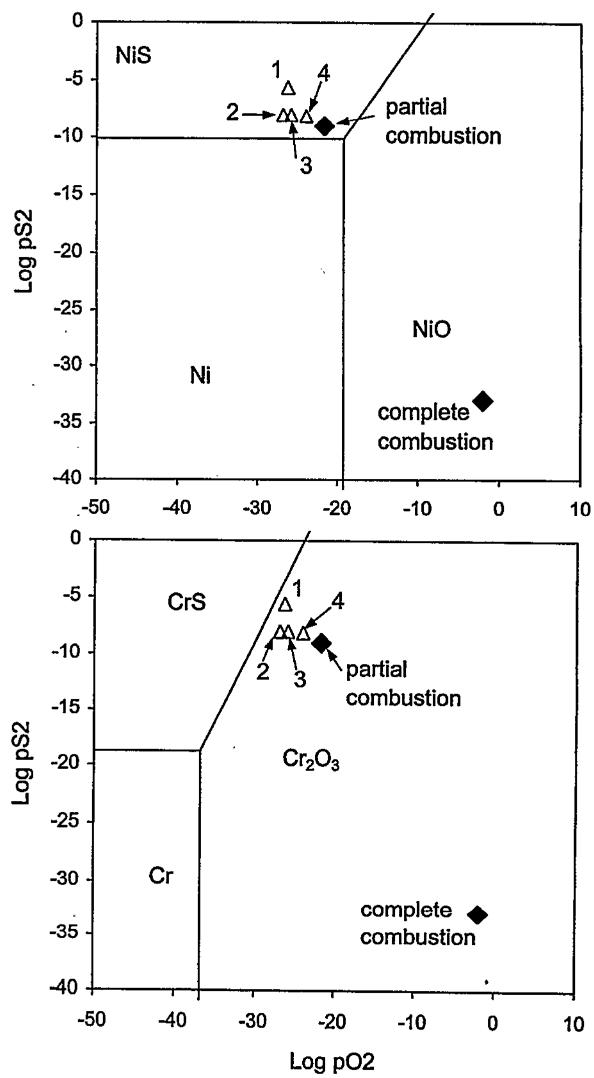

FIG. 1 Thermodynamically calculated equilibrium diagram for (a) the Ni-O-S systems and (b) the Cr-O-S systems at 600°C. Numbers in the pictures corresponds to the atmospheres.

Cast alloys tested were equiax IN-738LC, directionally solidified IN-738LC, and an experimental high chromium directionally solidified alloy (hereafter designated NiCr DS).

Derivatives of Waspaloy with modified chemistries were also tested. It seemed appropriate to modify the elements that effect grain boundary chemistry rather than bulk alloy chemistry, since the failures experienced in service progressed along grain boundaries. The majority of these Waspaloy modifications involved the reduction of carbon and increase of boron. Previous testing of U-720 in molten salt by the Westinghouse Research and Development Center had suggested that boron compounds along grain boundaries were more corrosion resistant than carbides. [4]

Waspaloy Bar, the first item listed in Table I, was used as a comparative standard during the testing. Approximately 258 kg

(569 pounds) of this heat was purchased per AMS 5704. Diameter of this bar was 15.8 mm (5/8 inch).

Waspaloy 11 through 41 were experimental ingots approximately 70 mm (2 ¾ inch) diameter rolled-down into 12 mm (1/2 inch) thick plates.

Waspaloy ER1 and ER2 were two heats provided by Allvac in the form of 15.8mm (5/8 inch) diameter bar.

All Waspaloy samples were solution treated, water quenched, aged at 845°C (1550°F) for 4 hours, and aged at 760°C (1400°F) for 16 hours.

U-720Li was 1104°C (2020°F) solution treated, water quenched, aged at 760°C (1400°F) for 8 hours, then aged at 649°C (1200°F) for 24 hours. The bar was 12mm (1/2 inch) diameter.

IN-738LC equiax and DS were cast as 16 mm (5/8 inch) diameter bars, 1185°C (2165°F) HIP processed, 1121°C (2050°F) solution treated, and 843°C (1550°F) aged for 24 hours. HIP of the DS alloy was not performed.

NiCr DS was directionally cast as 19 x 102 mm (0.75 x 4 inch) plate, 1204°C (2200°F) homogenized, 1079°C (1975°F) solution treated, and aged at 871°C (1600°F) for 20 hours. HIP was not performed.

TABLE I Chemistries of Alloys, Weight Percent

Alloy	C	Cr	Co	Mo	Al	Ti	B
Waspaloy Bar	0.068	19.21	13.50	4.10	1.40	3.13	0.006
Waspaloy 5	0.034	19.20	13.25	4.34	1.34	3.07	0.005
Waspaloy 6	0.032	19.18	13.25	4.03	1.32	3.08	0.004
Waspaloy 11	0.018	18.9	14.0	4.1	1.36	3.10	0.005
Waspaloy 12	0.018	18.9	14.0	4.1	1.35	3.10	0.030
Waspaloy 22	0.008	19.0	14.0	4.1	1.36	3.15	0.065
Waspaloy 41	0.010	19.0	14.0	4.1	1.36	3.15	0.011
Waspaloy ER1	0.039	19.72	13.43	4.32	1.30	3.00	0.015
Waspaloy ER2	0.034	19.71	13.35	4.27	1.32	2.96	0.013
X-750	0.04	16.7	0.14	0.07	0.8	2.42	
U-720 Li	0.011	16.3	14.1	2.9	2.43	5.0	0.014
IN-738LC	0.10	16.06	8.36	1.85	3.48	3.35	0.010
IN-738LC DS	0.09	16.20	8.7	1.8	3.4	3.5	0.009
NiCr DS		15	6		3.6	4.5	

Mechanical Properties

Solution heat treatment temperatures, grain sizes, room temperature tensile, and 732°C – 552 MPa (1350°F - 80 ksi) combination bar stress-rupture testing (Kt = 3.9 notch) results for the specimens were as shown in Table II. A "F" or "C" after the alloy name indicates that a sub-solvus fine grain (F) or super-solvus coarse grain (C) version of the chemistry was tested.

TABLE II Room Temperature Tensile and 732°C–552MPa (1350°F - 80 ksi) Stress-Rupture Properties in Air

Alloy	Solution Temp.	Grain Size	RT UTS (MPa)	RT Yield (MPa)	RT Elong.	SR Life	SR Elong.
Wasp. Bar	1038°C	5	1324	972	24 %	58 hr.	15 %
Wasp. 5	1025°C	6	1372	931	27 %	47 hr.	22 %
Wasp. 6-F	1004°C	9	1407	993	26 %	58 hr.	38 %
Wasp. 6-C	1052°C	4	1282	834	30 %	26 hr.	11 %
Wasp. 11	1024°C	4 & 9	1365	1007	30 %	75 hr.	29 %
Wasp. 12	1032°C	9	1441	1041	28 %	53 hr.	19 %
Wasp. 22	1032°C	9	1413	1000	28 %	25 hr.	9 %
Wasp. 41	1004°C	4 & 9	1365	979	29 %	36 hr.	23 %
Wasp. ER1	1018°C	9	1411	1024	28 %		
Wasp. ER2-F	1004°C	9	1379	965	26 %	49 hr.	35 %
Wasp. ER2-C	1052°C	3	1269	800	29 %		
X-750	Unknown	2	1117	662	16 %		
U-720 Li	1104°C	10	1703	1317	21 %		
IN-738LC	1121°C		1013	827	10 %		
IN-738LC DS	1121°C		1110	855	8 %		
NiCr DS	1079°C		1007	876	4 %		

Specimen Geometry & Sulfidation Test Results

Notched (N) gauge and Combination (C) gauge specimens of 3.8 mm (0.151 inch) diameter, Kt = 2.4, were used throughout this testing. Test atmospheres were air, hydrogen bubbled through room temperature water, and the mixed gas atmospheres 1, 2, 3, and 4 (See "Temperature, Equipment, & Procedure" heading). The atmosphere for each test is listed in the "Atm." column. Specimens that did not break display a "+" in the Life column. Results were as shown in Table III.

TABLE III Stress-Rupture Properties at 600°C in Selected Atmospheres

Test # (gauge)	Alloy	Atm.	Stress		Life	Fracture
1 (C)	Waspaloy Bar	Air	896 MPa	(130 ksi)	348 hr.	Smooth
2 (C)	Waspaloy Bar	Air	896 MPa	(130 ksi)	217 hr.	Smooth
3 (N)	Waspaloy Bar	1	517 MPa	(75 ksi)	169 hr.	Notch
4 (N)	Waspaloy Bar	1	689 MPa	(100 ksi)	55 hr.	Notch
5 (N)	Waspaloy Bar	1	689 MPa	(100 ksi)	35.5 hr.	Notch
6 (N)	Waspaloy Bar	1	689 MPa	(100 ksi)	43.6 hr.	Notch
7 (N)	Waspaloy Bar	1	689 MPa	(100 ksi)	43.6 hr.	Notch
8 (C)	Waspaloy Bar	1	689 MPa	(100 ksi)	33.9 hr	Notch
9 (C)	Waspaloy Bar	1	689 MPa	(100 ksi)	35.8 hr.	Notch
10 (C)	Waspaloy 5	1	689 MPa	(100 ksi)	148.5 hr.	Notch
11 (C)	Waspaloy 5	1	827 MPa	(120 ksi)	14.5 hr.	Notch
12 (N)	Waspaloy 11	1	827 MPa	(120 ksi)	300+ hr.	
13 (N)	Waspaloy 12	1	689 MPa	(100 ksi)	115+ hr.	
14 (N)	Waspaloy 22	1	827 MPa	(120 ksi)	300+ hr.	
15 (N)	Waspaloy 41	1	827 MPa	(120 ksi)	285 hr.	Notch
16 (C)	Waspaloy ER1	1	827 MPa	(120 ksi)	300+ hr.	
17 (N)	X-750	1	517 MPa	(75 ksi)	76 hr.	Notch
18 (N)	X-750	1	517 MPa	(75 ksi)	88 hr.	Notch
19 (C)	IN-738LC	Air	896 MPa	(130 ksi)	400+ hr.	
20 (N)	IN-738LC	1	689 MPa	(100 ksi)	8 hr.	Notch
21 (N)	IN-738LC	1	689 MPa	(100 ksi)	8.1 hr.	Notch
22 (N)	IN-738LC DS	1	689 MPa	(100 ksi)	3 hr.	Notch
23 (N)	NiCr DS	Air	517 MPa	(75 ksi)	500+ hr.	
24 (N)	NiCr DS	1	517 MPa	(75 ksi)	0.1 hr.	Notch
25 (N)	NiCr DS	H_2	517 MPa	(75 ksi)	200+ hr.	
26 (C)	Waspaloy Bar	2	689 MPa	(100 ksi)	18.4 hr.	Notch
27 (C)	Waspaloy Bar	2	689 MPa	(100 ksi)	16.2 hr.	Notch
28 (C)	Waspaloy Bar	3	689 MPa	(100 ksi)	106.0 hr.	Notch
29 (C)	Waspaloy Bar	3	758 MPa	(110 ksi)	39.6 hr.	Notch
30 (C)	Waspaloy Bar	3	758 MPa	(110 ksi)	42.4 hr	Notch
31 (C)	Waspaloy Bar	4	724 MPa	(105 ksi)	311.2 hr.	Smooth
32 (C)	Waspaloy Bar	4	758 MPa	(110 ksi)	51.9 hr.	Notch
33 (C)	Waspaloy Bar	4	793 MPa	(115 ksi)	54.2 hr.	Notch
34 (C)	Waspaloy Bar	4	793 MPa	(115 ksi)	47.2 hr.	Notch
35 (C)	Waspaloy Bar	4	862 MPa	(125 ksi)	25.4 hr.	Notch
36 (C)	Waspaloy Bar	4	862 MPa	(125 ksi)	26.2 hr.	Notch
37 (C)	Waspaloy Bar	4	862 MPa	(125 ksi)	55.7 hr.	Notch
38 (C)	Waspaloy Bar	4	862 MPa	(125 ksi)	85.2 hr.	Notch
39 (C)	Waspaloy Bar	4	896 MPa	(130 ksi)	23.1 hr.	Notch
40 (C)	Waspaloy 6-F	4	827 MPa	(120 ksi)	52.3 hr.	Smooth
41 (C)	Waspaloy 6-F	4	862 MPa	(125 ksi)	114.5 hr.	Smooth
42 (C)	Waspaloy 6-F	4	931 MPa	(135 ksi)	47.5 hr.	Smooth
43 (C)	Waspaloy 6-C	4	862 MPa	(125 ksi)	2.4 hr.	Notch
44 (C)	Waspaloy 22	4	862 MPa	(125 ksi)	2.0 hr.	Notch
45 (C)	Waspaloy 41	4	862 MPa	(125 ksi)	16.4 hr.	Notch
46 (C)	Waspaloy ER2-F	4	862 MPa	(125 ksi)	27.4 hr.	Smooth
47 (C)	Waspaloy ER2-F	4	862 MPa	(125 ksi)	45.8 hr.	Smooth
48 (C)	Waspaloy ER2-C	4	862 MPa	(125 ksi)	15.2 hr.	Smooth

49 (C)	X-750	4	689 MPa	(100 ksi)	9.8 hr.	Smooth
50 (C)	U-720 Li	4	862 MPa	(125 ksi)	14.5 hr.	Notch
51 (C)	U-720 Li	4	931 MPa	(135 ksi)	23.5 hr.	Notch
52 (C)	IN-738LC	4	586 MPa	(85 ksi)	54.4 hr.	Notch
53 (C)	IN-738LC	4	689 MPa	(100 ksi)	4.9 hr.	Notch
54 (C)	IN-738LC	4	793 MPa	(115 ksi)	4.6 hr.	Smooth
55 (C)	IN-738LC	4	862 MPa	(125 ksi)	0.1 hr.	Smooth
56 (C)	NiCr DS	4	689 MPa	(100 ksi)	0.1 hr.	Notch

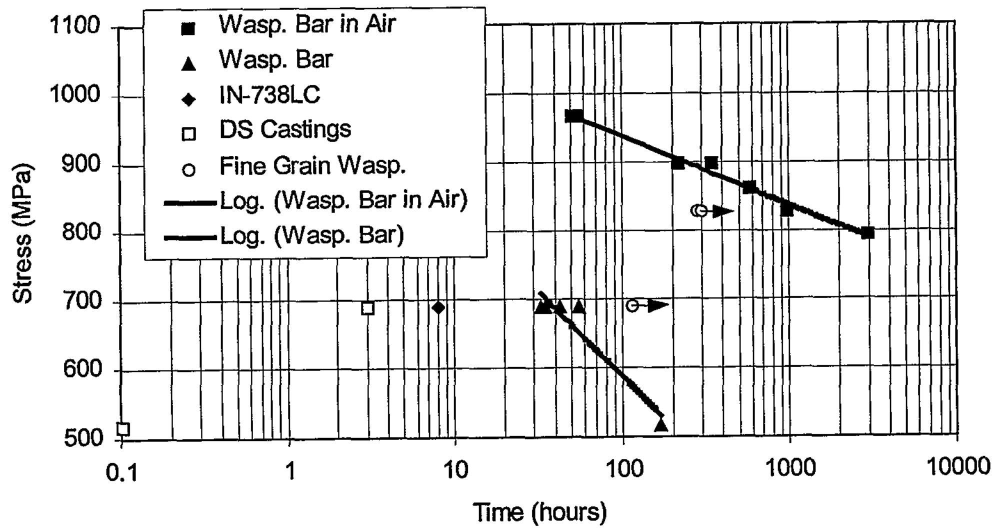

FIG.2. Semi-log plot of stress-rupture data at 600 °C (1112 °F) in atmosphere 1, i.e., log O_2 = -26.3 and log S_2 = -5.6, except where stated in air.

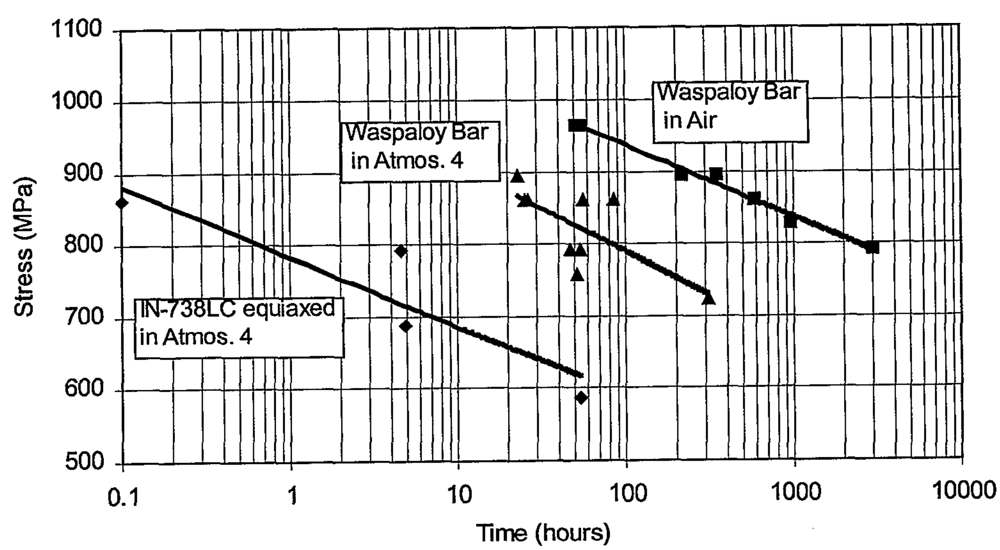

FIG.3. Semi-log plot of stress-rupture data at 600 °C (1112 °F) in air and atmosphere 4, i.e., log O_2 = -24.0 and log S_2= -8.1.

The semi-log plots produced from the rupture data revealed some interesting observations (Figs. 2 & 3). The most striking result was that the wrought alloys outperformed the cast alloys. The high performers in atmosphere 1 were fine grained wrought alloys. In atmosphere 4 these same fine grained alloys produced varied results. Rupture life data scatter was also larger in atmosphere 4.

Analysis of Waspaloy Surface Scales

Surface scales on the Waspaloy specimens were visually examined (Fig. 4). Atmosphere 1 produced gold colored bright crystalline surface scales, occasionally peppered by small gold colored nodules. Atmosphere 4 produced gold colored surface scales that were frequently covered with thick gray-green powdery nodules. The gold scale of atmosphere 1 had the color of pyrite, while the gold scale of atmosphere 4 displayed a tint of olive green. Both gold scales were crystalline and seemed epitaxial. The crystals formed in atmosphere 1 could easily be misinterpreted as intergranular fracture features (Fig. 5). The gray-green scale formed in atmosphere 4 was more porous and had the appearance of sponge coral composed of fine crystals (Fig. 6).

Energy Dispersive Spectroscopy (EDS) revealed the gold scales, gold nodules of atmosphere 1, and gray-green powdery nodules of atmosphere 4 were composed of 48-60% nickel, 27-41% sulfur, 6-12% cobalt, and 0-6% oxygen in atomic percent. As throughout this paper these percentages were determined by standardless quantitative analysis using an EDAX DX' system.

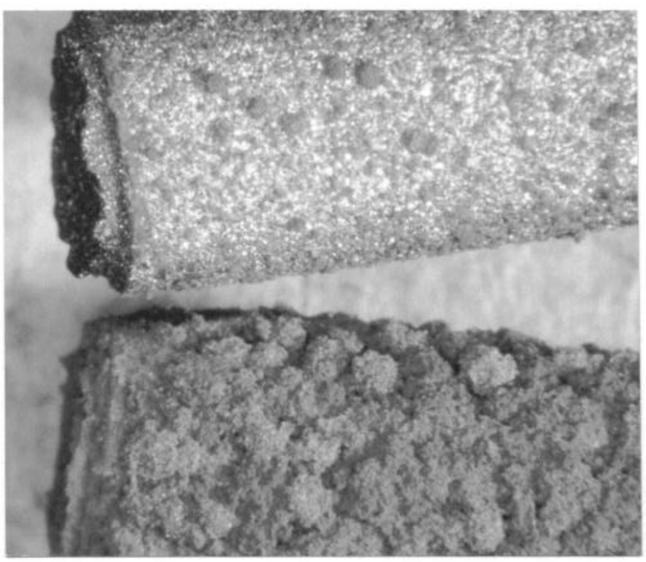

FIG. 4 Two Waspaloy Bar specimens after fracturing through the notch during testing. The top specimen was subjected to Atmosphere 1 for 43.6 hours. The bottom specimen was subjected to Atmosphere 4 for 26.2 hours. (Mag. 10X)

Many of the specimens were longitudinally sectioned, and a few were examined in the SEM. Longitudinal sectioning revealed the characteristic two layered scale (Fig. 7). Appearance of the inner scale immediately adjacent to the base metal was light gray, and appearance of the outer scale was gold. The gray-green nodules of atmosphere 4 not only had the same chemistry as the gold surface scales, but were revealed to be the peaks of the gold scales. Optical appearance of the gray-green nodules had apparently been effected by the fine crystal size. Further examination using backscatter SEM imaging revealed the outer scale consisted of two phases, a Ni_xS_y phase and a $(Ni,Co)_xS_y$ phase.

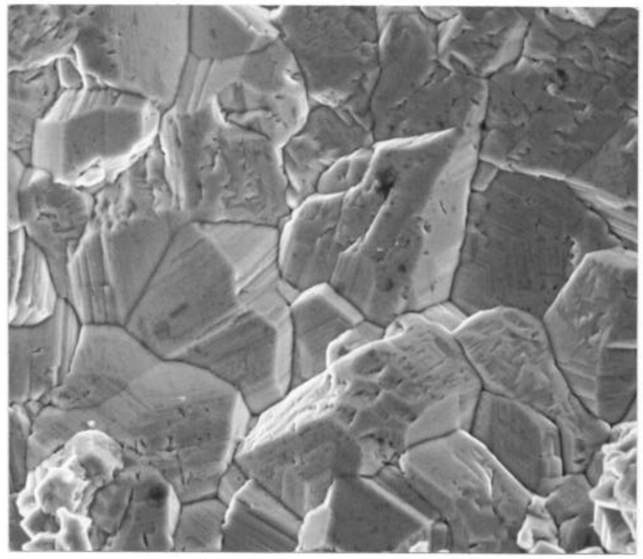

FIG. 5 SEM image of the gold colored surface scale produced in atmosphere 1. (Mag. 1,000X)

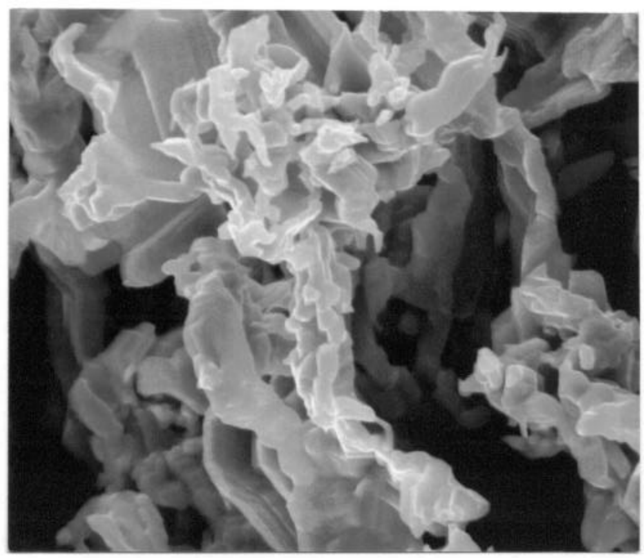

FIG. 6 SEM image of the gray-green porous scale produced in atmosphere 4. Sharp corners on the crystals confirmed that 635°C was not exceeded during the test. (Mag. 3,000X)

EDS of the inner scale revealed different chemistries for atmospheres 1 & 4. Atmosphere 1 inner scale consisted of approximately 22% chromium, 52% sulfur, 14 % oxygen, 5% titanium, 4% aluminum, 2% nickel, and 1% cobalt in atomic percent. Atmosphere 4 inner scale consisted of approximately 28% chromium, 18% sulfur, 33% oxygen, 5% titanium, 5% aluminum, 6% nickel, and 4% cobalt in atomic percent. The higher sulfur and lower oxygen content of atmosphere 1, did produce an inner scale with a higher sulfur : oxygen ratio.

Sulfur to oxygen ratios of the inner scale for Waspaloy were 3.7:1 in atmosphere 1, and 0.5:1 in atmosphere 4.

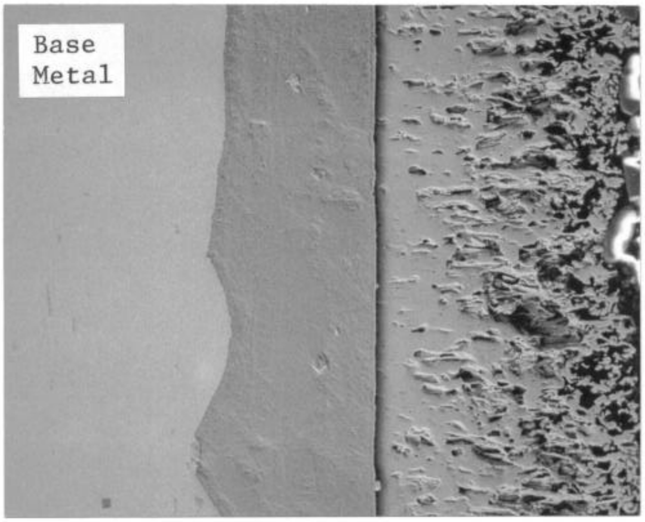

FIG. 7 Longitudinal section of a Waspaloy Bar specimen. SEM backscatter imaging reveals the outer scale as a continuous growth extending outward from the inner scale. Base metal carbides were evident in the inner scale. (Mag. 250X)

Carbides visible in the inner scale suggested that the interface between the inner scale and the outer scale was the original gauge diameter of the specimen prior to testing. The Waspaloy Bar specimen that had survived for 311.2 hours in atmosphere 4 was cross-sectioned. Diameter of the specimen prior to testing was 3.84 mm (0.151 inch). After testing, diameter of the inner scale / outer scale interface was 3.76 mm (0.148 inch), and the diameter of the base metal / inner scale interface was 3.63 mm (0.143 inch). Cross-section reduction as a result of sulfidation had resulted in a 10% increase in specimen stress during the duration of the test.

The inner scale / base metal interface was not perfectly straight. Blunt intrusions of inner scale were evident along the length of each specimen. A few of these intrusions exhibited the beginnings of a very localized attack into the grain boundaries (Fig. 8). No grain boundary attacks greater than 0.025 mm (0.001 inch) were detected, thereby suggesting that once preferential grain boundary attack began it continued very rapidly until failure.

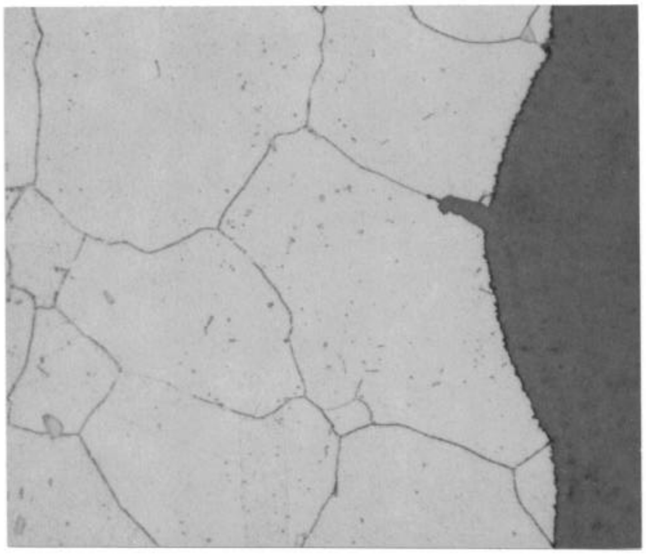

FIG. 8 Longitudinal section of a Waspaloy Bar specimen. The beginning of grain boundary attack is evident. (Mag. 500X)

Discussion of Waspaloy Specimens

Waspaloy Bar, the comparative standard, fractured through the notch in every sulfidation test except one. The one test that produced a smooth gauge failure was in atmosphere 4 at 724 MPa (105 ksi). Longitudinal sectioning of the Waspaloy Bar specimens confirmed the fracture mode in all cases was intergranular (Fig. 9).

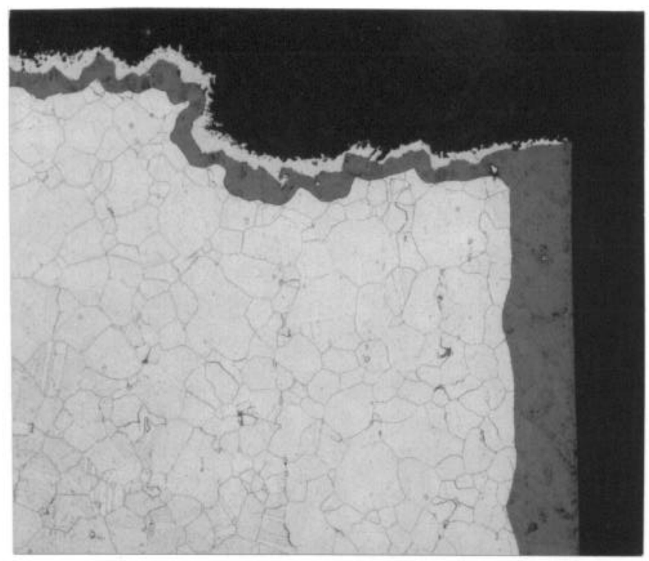

FIG. 9 Longitudinal section of a Waspaloy Bar specimen. Fracture was intergranular. Outer scale had flaked off gauge diameter. Grain size ASTM E112 No. 5. (Mag. 100X)

Waspaloy 5 and Waspaloy 6 had nearly identical chemistries within the normal acceptance limits for Waspaloy. The grain size ASTM E112 No. 4 version fractured through the notch in 2.4 hours in atmosphere 4. The grain size ASTM E112 No. 6 and 9 versions performed equal to or better than Waspaloy Bar in atmospheres 1 & 4.

Discussion of Modified Waspaloy Specimens

Chemically modified Waspaloy specimens were tested in atmosphere 1 and revealed encouraging results. These modified chemistries, and the standard chemistry of Waspaloy 11, had all been sub-solvus heat treated and were either a uniform ASTM E112 No 9 grain size or were of a necklace microstructure containing ASTM E112 No. 9 grains. Grain size in this atmosphere played a larger role in sulfidation resistance than alloy chemistry. It could be speculated that spreading out the desirable or undesirable grain boundary constituents, such as carbon or selenium, among more and more grain boundaries, resulted in grain boundaries that were less susceptible to sulfidation attack.

Fine grain size did not enhance stress-rupture life in atmosphere 4. The only benefit a fine grain size provided in this environment was a tendency toward smooth gauge rupture. The modified chemistry most detrimentally effected by atmosphere 4 was the carbon lean, high boron, Waspaloy 22. This fine grained alloy survived 300 hours in atmosphere1, but fractured after only 2 hours in atmosphere 4.

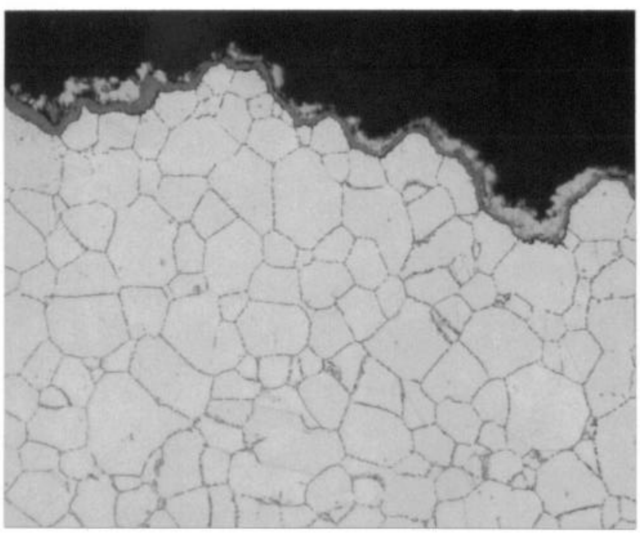

FIG. 10 Longitudinal section of a Waspaloy ER specimen. Fracture was intergranular. (Mag. 500X)

Waspaloy 41 and the two Allvac ER heats, ER1 and ER2, had similar chemistries, with the most significant difference being that Waspaloy 41 had approximately 1/3 the carbon content of the Waspaloy ER grades. This lean amount of carbon seemed to detrimentally effect stress-rupture life in atmosphere 4. The Waspaloy ER grade was also interesting in that fracture always occurred through the smooth gauge rather than the notch, no mater what grain size was tested (Fig. 10).

Discussion of X-750 Specimens

X-750 has lower stress-rupture strength compared to Waspaloy in air, and was not expected to outperform the Waspaloy material in the sulfidation atmospheres. Stress-rupture lives of X-750 specimens in atmospheres 1 & 4 were shorter than that of the Waspaloy Bar specimens at equivalent stress. Fracture of X-750 in both test atmospheres was intergranular.

Discussion of U-720Li Specimens

Udimet 720Li is a high strength, fine grain, superalloy with lower carbon and higher boron content than commercially available Waspaloy. Westinghouse research on the corrosion behavior of Udimet 720 (higher carbon, chromium, and boron version of this alloy) in molten salt had revealed superior sulfidation resistance.[4] During this testing, however, stress-rupture life of U-720Li in atmosphere 4 seemed no better than Waspaloy Bar. Fracture of U-720Li was intergranular and originated at the notch (Fig. 11).

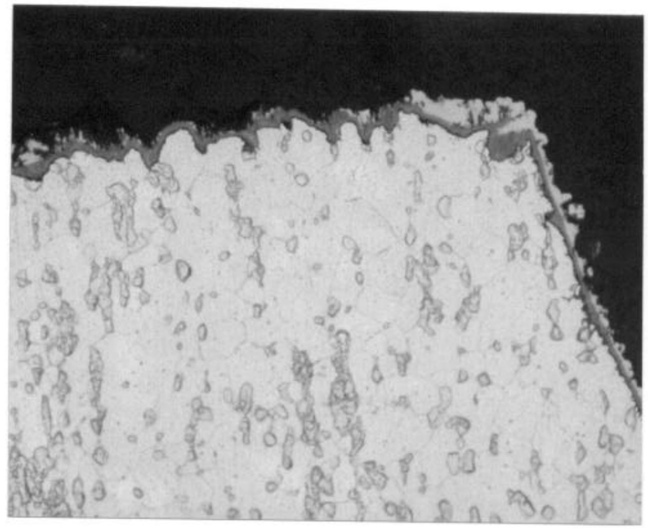

FIG. 11 Longitudinal section of a U-720Li specimen. Fracture was intergranular. (Mag. 500X)

Discussion of IN-738LC Equiax Cast Specimens

Conventionally cast IN-738LC performed exactly the same in atmosphere 1 & 4. Fracture of these specimens occurred along cast grain boundaries (Fig. 12). Fracture topography was dendritic. EDS of the outer scales revealed 42-57% nickel, 40-46% sulfur, 3-5% cobalt, 3-5% chromium, and 0-3% oxygen in atomic percent.

EDS of the inner scale formed in atmosphere 1 was approximately 15% chromium, 47% sulfur, 15% oxygen, 5% titanium, 12% aluminum, 2% nickel, 2% tungsten, and 2% tantalum. EDS of the inner scale formed in atmosphere 4 was approximately 17% chromium, 34% sulfur, 23% oxygen, 6% titanium, 10% aluminum, 5% nickel, 2% tungsten, and 2% tantalum.

Sulfur to oxygen ratios of the inner scale for IN-738LC were 3.1:1 in atmosphere 1, and 1.5:1 in atmosphere 4.

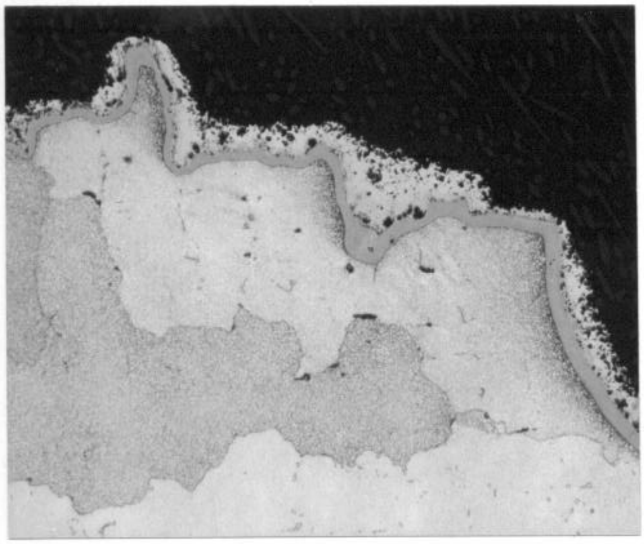

FIG. 12 Longitudinal section of an IN-738LC equiax specimen. Fracture occurred along the cast grain boundaries. (Mag. 100X)

Discussion of DS Cast Specimens

It was anticipated that significant stress-rupture life in the sulfidation atmospheres could be achieved by aligning the grain boundaries parallel to the direction of stress. Two high chromium directionally solidified alloys were selected. These alloys were IN-738LC and NiCr, a proprietary high chromium alloy. Neither alloy was HIP processed. Both alloys performed very poorly. Fracture of these specimens occurred through the notch in 2 minutes to 3 hours. The fractures initiated and progressed a short distance perpendicular to the direction of applied stress, then transitioned to dendrite arm boundaries (Figs. 13 & 14). Several origins were evident around the gauge diameter of the specimens.

To determine if these short failure times were due solely to the presence of atmospheric sulfur, a test using pure hydrogen bubbled through room temperature water was performed. This hydrogen test did not cause failure in 200 hours. It was concluded that DS alloys have a crystallographic plane extremely susceptible to sulfidation in atmospheres 1 & 4.

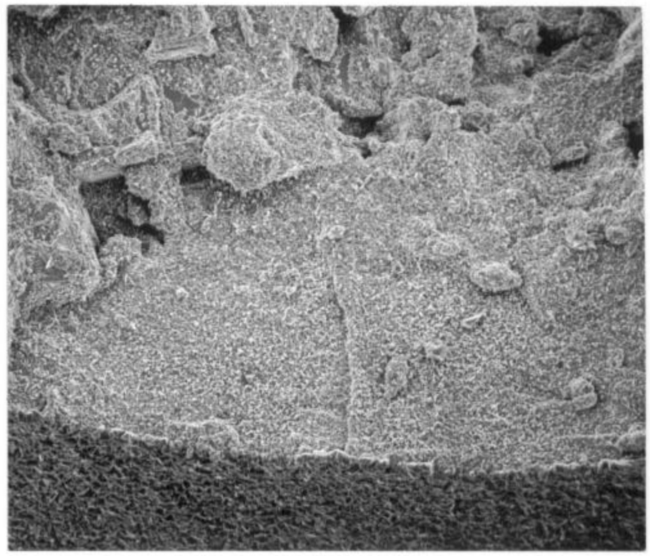

FIG. 13 Fracture surface of the NiCr DS specimen tested in atmosphere 4. Fracture initiation was flat, along what appears to be crystallographic planes, then shifted to dendritic. (Mag. 200X)

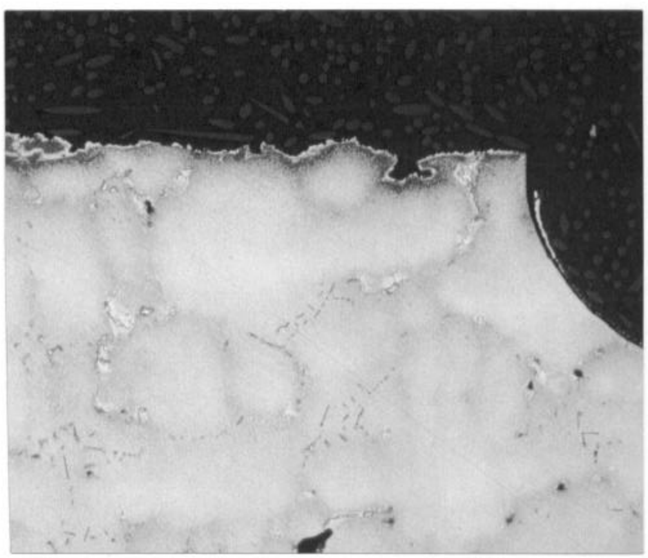

FIG. 14 Longitudinal section of the IN-738LC DS specimen tested in atmosphere 1. Fracture initiated perpendicular to the direction of applied stress, then progressed along dendrite arm boundaries. (Mag. 100X)

Conclusions

1. Nickel base precipitation strengthened superalloys can suffer significant stress-rupture life reductions at temperatures below the 635°C (1175°F) nickel sulfide eutectic. These life reductions are possible in low pO_2 environments containing significant pS_2.

2. Surface scales that formed on the test specimens in atmospheres 1 & 4 consisted predominantly of an outer scale of nickel sulfide, and a mixed inner scale of chromium sulfide / chromium oxide. The ratio of sulfur : oxygen in the inner scale of each alloy was effected by the ratio of sulfur : oxygen in the test atmosphere.

3. Stress-rupture life of the wrought alloys, Waspaloy and U-720Li, was notably longer than the cast alloys, IN-738LC and IN-738LC DS, in the sulfidation atmospheres.

4. Grain size refinement of Waspaloy significantly increased the 600°C (1112°F) stress-rupture life of specimens tested in atmosphere 1.

5. Current understanding of this sulfidation fracture mode is that it begins with the outward diffusion of nickel from the base metal to form a crystalline nickel sulfide outer surface scale. Sulfur and oxygen replace the depleted nickel to form an inner scale of chromium sulfide / chromium oxide. Shallow spikes then preferentially attack the grain or dendrite boundaries and cause rapid separation.

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