SULFIDATION

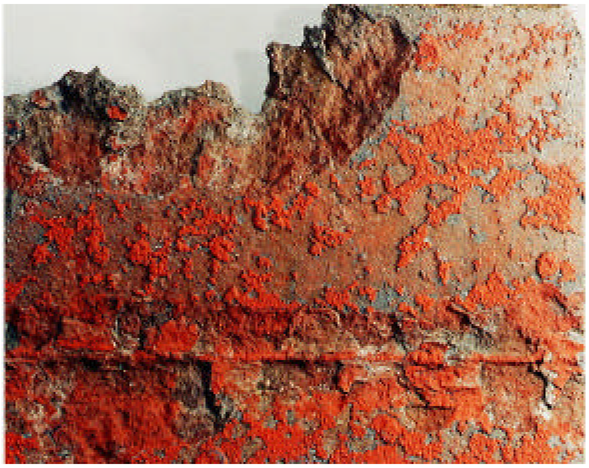
Environments containing sulfur may rapidly attack high nickel alloys. The problem is more severe under reducing, or low oxygen, environments. The higher the nickel the more sensitive the alloy is to sulfidation attack. If sulfur is a problem, we do not suggest using any alloy with more than 20% nickel. RA310, with 25% chromium and 20% nickel, is useful in many sulfur bearing environments. RA309, at 13% nickel, may be preferred for some applications. Under the most severe conditions an alloy completely free of nickel, such as RA446 may be required, in spite of other disadvantages it has.

When the environment is oxidizing the alloy is more likely to form a protective chromium oxide scale, rather than a chromium sulfide. Under reducing environments the alloy forms chromium sulfide, which is non-protective.

An oxidizing environment is one in which sulfur is present as sulfur dioxide (SO_2), and there is some excess oxygen (O_2), or even carbon dioxide (CO_2) and/or water vapor (H_2O). In reducing environments sulfur is in the form of hydrogen sulfide (H_2S), there may be hydrogen (H_2), carbon monoxide (CO), methane (CH_4) or other sources of carbon, and rather little CO_2 or H_2O.

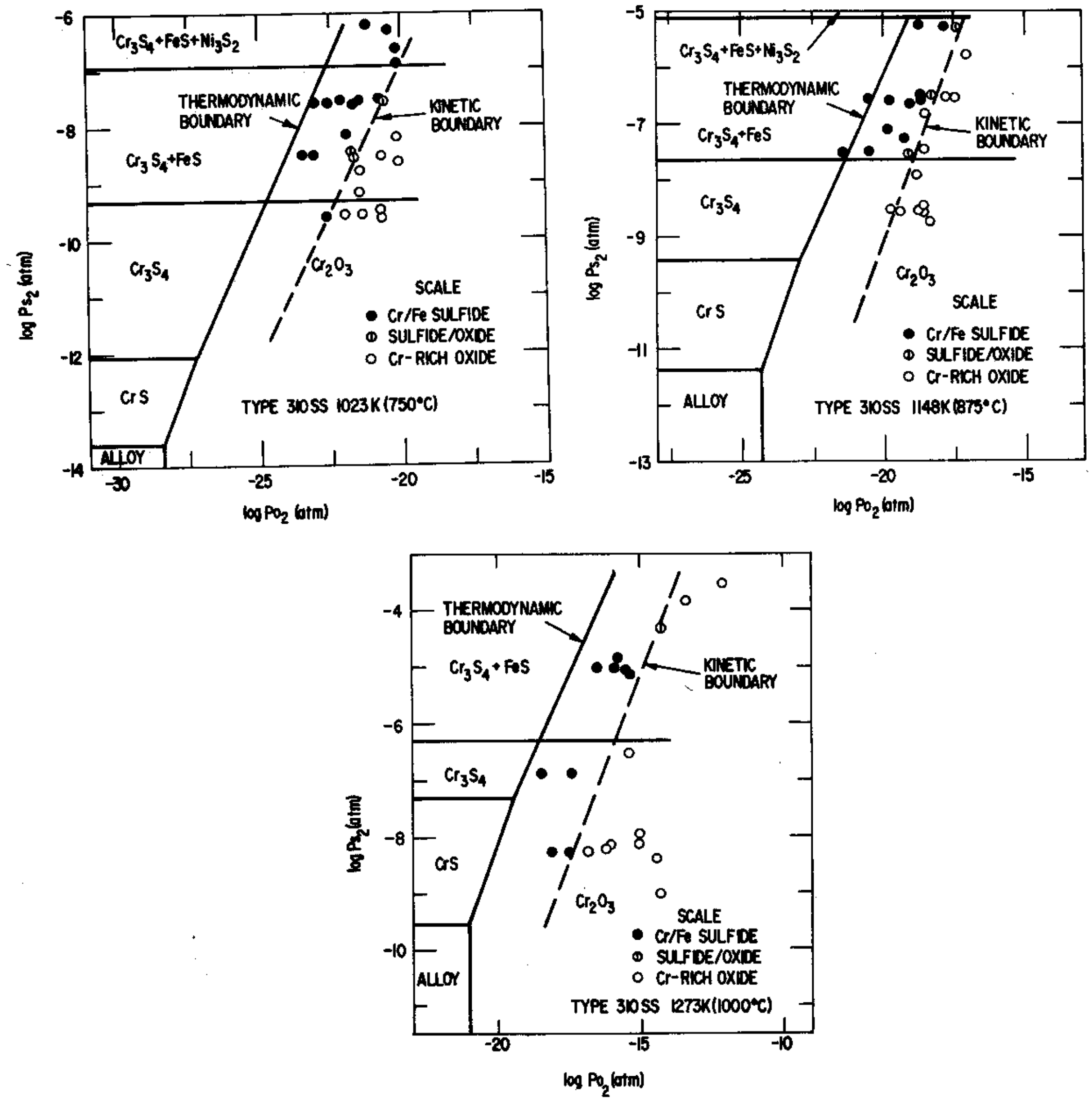
Sometimes the distinction isn't obvious. For example, there may be solid deposits on metal in an oxidizing environment. Underneath those deposits, in contact with the metal the actual amount of oxygen available to form a scale is miniscule. It has been stated that oxygen partial pressures may be about 10^{-8} under calcium sulfate deposits on fluidized bed components. If the deposit contains sulfur, then the metal may be heavily attacked under the deposit, regardless of oxygen is in the atmosphere above it.

An example of under deposit attack is shown below. This 1/4" (6.35mm) RA 253 MA plate sample came from a kiln processing ferrous sulfate monohydrate to red iron oxide pigment. The atmosphere was air, plus the SO_2 and SO_3 driven off in the process, operating temperature 1840°F (1004°C). After about a year the RA 253 MA kiln shell had developed holes roughly 3/4" (20mm) across, some rather long. Previously used RA310 had failed by more uniform thinning, and lasted 2 to 2 1/2 years.



From Rolled Alloys Report Number 94-72

Sulfidation, continued



Types of Scale Developed on Type 310 Stainless Steel as a Function of Oxygen and Sulfur Partial Pressures in the Gas Environment at Temperatures of 750, 875, and 1000C. Conversion factor: 1 atm = 0.101356 MPa. ANL Neg. No. 306-79-625[1] These diagrams illustrate whether oxides or sulfides are formed at equilibrium.

"For a given sulfur partial pressure, there exists a threshold value for oxygen partial pressure beyond which a continuous protective oxide scale is developed on the specimens. This threshold oxygen partial pressure, represented by the kinetic boundaries in the figure, is ~10^3 times the oxygen partial pressure for he Cr oxide/Cr sulfide equilibrium." In our opinion, Dr. K. Natesan of Argonne has done, and continues to do, the best high temperature corrosion work of our time.

The meaning of these diagrams is simply that if not enough oxygen is present, or the sulfur is too high, the alloy will form a chromium sulfide rather than an oxide. While the oxide may be protective, the sulfide offers little resistance to further attack.

Sulfidation, continued

Nickel reacts chemically with sulfur very readily. Unlike metal oxides, which at least are solid, metal sulfides, or metal-metal sulfide eutectics, are often molten at operating temperature. If sufficient molten metal sulfide forms underneath the chromium oxide scale, it may literally wash that scale away. Useful corrosion testing for sulfidation resistance requires very long time exposure. In general, the corrosion rate in sulfidation may be more or less parabolic for some period of time. Eventually, corrosion enters a "break-away" mode[2], where corrosion rates accelerate dramatically.

The most comprehensive study of heat resistant alloy sulfidation was carried out in the late 1970's through early 1980's under the direction of the Metals Properties Council. Some of their results, from the 1987 Final Report, are included here. We present Table 8 from that report, time to breakaway corrosion. This is, in our view, the significant measure of sulfidation resistance.

ESTIMATED TIME TO BREAKAWAY CORROSION FOR VARIOUS ALLOYS
Based on Metallographic Measurements and Gravimetric Analysis in 1000 psig Tests

		Estimated Time, 1000 hour							
		1650°F— 0.5 vol% H_2S		1650°F— 1.0 vol% H_2S		1800°F— 0.5 vol% H_2S		1800°F— 1.0 vol% H_2S	
Alloy	**Wt % Cr**	**Met.**	**Grav.**	**Met.**	**Grav.**	**Met.**	**Grav.**	**Met.**	**Grav.**
671	50.2	>10	>10	>10	>10	>10	>10	>10	>10
657	48.0	>10	>10	>10	>10	>10	>10	>10	>10
HL-40[A]	30.9	>10	>10	3	2	>10	>10	>10	>10
Co-Cr-W No. 1	30.0	>10	>10	>9	>9	>10	>10	>10	>10
T63WC[B]	28.2	>10	>10	2	4	>10	>10	>10	8
6B	28.1	>10	>10	>10	>10	>10	>10	>10	>10
HK-40[A]	28.0	>10	>10	2	1	1	1	7	5
30/50W[B]	27.9	- -	- -	- -	- -	- -	- -	>10	>10
RA333	26.2	>10	>10	>8	7	5	4	2	2
Crutemp 25	25.4	>10	>10	>10	3	>10	>10	>8	6
310	25.0	<10	3	10	10	1	<1	- -	- -
310 (Al)	25.0	>10	>10	10	>10	>10	>10	>10	>10
446	24.0	>10	>10	- -	- -	>4	1	2	c
309	23.0	3	2	<1	<1	3	4	- -	- -
188	22.0	5	>10	3	3	10	>10	<1	1
556	22.0	>10	>10	1	1	- -	- -	- -	- -
617[B]	22.0	10	>10	1	<1	>8	>8	3	4
Alloy X	21.9	>10	>10	>10	>10	10	>10	1	1
32X	21.6	<5	4	5	6	1	1	- -	- -
N-155	20.9	>10	>10	>10	>10	>10	>10	>10	9
800H	20.6	>10	10	8	7	6	- -	- -	- -
800H (Al)	20.6	>10	>10	>10	>10	>5	>5	10	>10

Sulfidation, continued

Alloys Tested

Alloy Name	UNS	Alloy Compositions							
		Cr	Ni	Co	W	Mo	Si	C	Fe	Other
671	R20500	50.20	47.80	- -	- -	- -	0.39	0.06	1.10	0.24Ti
IN-657[A]	R20501	48.00	50.00	- -	- -	- -	- -	- -	- -	1.5Cb
HL-40	J94614	30,90	19.40	- -	- -	0.01	1.40	0.47	47.10	0.60Mn
Co-Cr-W No. 1	R30001	30.0	- -	55.50	12.0	- -	- -	2.50	- -	- -
Thermalloy® 63WC	- -	28.20	36.00	15.00	5.0	- -	1.40	0.52	13.78	0.10Mn
Stellite® 6B	R30106	28.10	2.80	57.10	4.8	1.20	0.50	1.00	1.90	1.40Mn
HK-40[A]	J94204	28.00	20.00	- -	- -	0.50	2.0	0.40	47.10	2.00Mn
Wiscalloy® 30/50W	- -	27.90	48.70	- -	3.6	- -	1.00	0.51	17.42	0.87Mn
RA333®	N06333	26.20	45.00	2.50	2.7	3.80	1.40	0.05	15.50	1.50Mn
Crutemp® 25	- -	25.40	24.80	- -	- -	0.40	0.60	0.07	47.20	1.50Mn
310	S31008	25.00	20.20	- -	- -	- -	0.68	0.06	52.20	1.71Mn
310 (Al)	S31008	25.00	20.20	- -	- -	- -	0.68	0.06	52.20	1.71Mn
446	S44600	24.00	0.40	- -	- -	- -	0.38	0.10	74.60	0.45Mn
309	S309008	23.00	14.70	- -	- -	- -	0.11	0.11	62.50	0.54Mn
Haynes® 188	R30188	22.00	22.90	37.96	14.5	0.60	0.40	0.09	1.20	0.06Mn 0.22Al 0.07La
556[A]	R30556	22.00	20.00	20.00	2.5	3.00	0.40	0.10	29.18	1.50Mn 1.1Cb+Ta 0.30Al 0.02La
617[A]	N06617	22.00	54.00	12.50	- -	8.00	- -	0.07	- -	1.00Al
Alloy X	N06002	21.90	44.60	2.50	0.5	9.10	0.44	0.09	19.50	0.69Mn 0.21Al
Sanicro® 32X	- -	21.60	32.00	- -	3.1	- -	1.10	0.10	40.72	0.65Mn 0.40Al 0.33Ti
N-155®, Multimet®	R30155	20.90	19.80	19.50	2.8	3.00	0.60	0.10	29.00	1.30Mn 1.1Cb+Ta
800H	N08810	20.35	30.00	- -	- -	- -	0.23	0.08	46.13	0.94Mn 0.37Al 0.38Ti 0.72Cu
800H (Al)	N08810	20.35	30.00	- -	- -	- -	0.23	0.08	46.13	0.94Mn 0.37Al 0.38Ti 0.72Cu

[A]**Nominal chemistry only**

(Al) means the sample was aluminum diffusion coated. This test data gives an indication of how much sulfur heat resistant alloys might tolerate at what temperature in a mildly reducing atmosphere. What it says about alloys is that high chromium, at least 25%, is necessary for any degree of sulfidation resistance. It does not indicate how materials might perform under deposits. In the pilot plant exposure part of this test series, alloy 671 sulfidized badly beneath calcium sulfate deposits. RA333, chosen for an oil sands pilot project on the basis of early good results, sulfidized beneath carbon deposits.

The reaction vessels were aluminum diffusion coated 310, burned out after every 1000 hour run.

Sulfidation, continued

The test atmosphere supplied to the reactor for CGA (coal gasification atmosphere) was borderline oxidizing-reducing, from Table A-1 shown below:

Inlet Gas Atmosphere
for Initial Tests

Gas	vol%
CO_2	12
CO	18
H_2	24
CH_4	5
HN_3	1
H_2S	1.0, 0.5, or 0.1
H_2O	Balance

Many sulfidation failures occur under highly reducing conditions. That is, where a source of carbon, such as methane (CH_4) is present along with the hydrogen sulfide Even 1/2% of H_2S can be quite destructive. One example is in carbon black manufacture. Low-grade oil is heated with very little oxygen to break it down into soot—which is carbon— or lamp black. The oil used as feed-stock normally contains up to 3 percent sulfur. High nickel alloys are quite unsuited for high temperature service in the sulfidizing environments of carbon black plants. Specifically, RA330, RA333, alloys X, 800H, 600, 601, 617 and some of the high cobalt alloys may fail by sulfidation.

Melting points of some metal-metal sulfide eutectics are[3] : 1175°F (635°C) for Ni-Ni_3S_2, 1611°F (877°C) for Co-Co_4S_3 and 1810°F (988°C) for Fe-FeS. The Fe0-FeS eutectic melts at 940C[4] . CrS-Cr_2S_3 doesn't melt until 2462°F (1350°C)[5].

References

1. K. Natesan, *CORROSION AND MECHANICAL BEHAVIOR OF MATERIALS FOR COAL GASIFICATION APPLICATIONS*, ANL-80-5, Argonne National Laboratory, Argonne, Illinois U.S.A. 1980

2. Maurice A. H. Howes, *High-Temperature Corrosion in Coal Gasification Systems*, Final Report (1 October 1972-31 December 1985) as subcontractor to The Materials Properties Council, Inc., New York, New York.

3. *Binary Alloy Phase Diagrams*, Thaddeus B. Massalski, Editor, 1986, American Society for Metals, Metals Park, Ohio

4. Stanislaw Mrowec, Teodor Werber, *Gas Corrosion of Metals,* translation published by the Foreign Scientific Publications Department of the National Center for Scientific, Technical and Economic Information, Warsaw, Poland 1978

5. *Handbook of Chemistry and Physics, 65th Edition,* CRC Press Inc., Boca Raton, FL 1984—1985