

MOLTEN SALT CORROSION

When Ni-20Cr alloys and stainless steels are oxidized while submerged in molten salt (NaCl or NaCl-KCl), readily oxidizable alloy components, such as chromium, and in some cases iron, migrate to the surface to form non-adherent, granular and thus nonprotective oxides. This loss of alloy constituents causes a counter current flow of vacancies which condense into an interconnecting pore network filled with salt. Since the salt penetrates into the structure, the loss of alloying metals does not require intermetallic diffusion over long distances, but instead corrosion products are largely removed by solution of alloying metals as ions in the pre-salt network . . .chromium diffuses down grain boundaries of the grain network to be deposited at grain boundary-pore intersections as chromium ions. The concentration gradient of chromium ions in the salt phase forces chromium diffusion out to the bulk salt where the higher effective oxygen pressure forms Cr_2O_3 and some chromate ion.

A. U. Seybolt, Oxidation of Ni-20Cr Alloy and Stainless Steels in the Presence of Chlorides, Oxidation of Metals, Vol. 2, No. 2, 1970

Hot chloride salts, and particularly salt fumes mixed with air, are very corrosive to heat resistant alloys. In general the higher nickel alloys, such as 600, are preferred, although we have seen tolerable results from the 1.7% silicon grade, RA 253 MA.

Corrosion in Molten Chloride Heat Treat Salts, 1100-2200°F (600-1200°C)

Depth of Intergranular Attack

Grade	Nickel, weight %	Silicon, weight %	mm	inch
RA85H	15	3.5	0.11	0.0044
RA 253 MA	11	1.7	0.18	0.0069
RA600	76	0.2	0.19	0.0075
RA309	13	0.8	0.32	0.0125
RA330	35	1.2	0.35	0.0138

Plate samples were exposed in a commercial heat treat salt line. They saw 210 to 252 cycles in preheat salts 700°C (1290°F) and 815°C (1500°F), high heat salt 1200°C (2200°F), quench in 600°C (1100°F) nitrate/nitrite salt, air cool. Preheat and high heat salts were mixtures of potassium, sodium and barium chlorides.

The alkali metals in the salt turn the protective chromium oxide scale into an alkali chromate, which is non-protective and water soluble. As fast as the scale is removed, more chromium diffusing to the surface reforms the scale. Eventually most of the chromium may be removed from the alloy, leaving primarily iron and nickel.

A more detailed account of hot salt corrosion mechanisms is given under Neutral Salt Pots, 13-16.

Molten Salt Corrosion, continued

Fluoride salts are more aggressive than are chloride salts. Molten fluorides are used to flux metals and alloys for brazing operations. Along with fluxing the oxide film on the workpiece, fluorides also attack the chromium oxide film on heat resistant alloy fixturing. A service trial of various alloy fixtures used in aluminum salt bath brazing at 1125°F (607°C) gave the following results:

Alloy	Total Life, days
RA333	197 (end of test—no failure)
600	112
Nickel 200	51
C-276	40
601	14

Other work has shown the 25% chromium ferritic grade, RA446, to be unsuitable for aluminum salt bath brazing operations.

Vanadium Pentoxide

Equipment fired with residual fuel oil suffers corrosion wherever the fuel ash deposits on hot metal. Heavy oils such as No. 6 or “Bunker C” may contain both sulphur and vanadium. When this oil is burned, the vanadium forms vanadium pentoxide, V_2O_5 . This vanadium pentoxide, along with sodium sulfate, makes a molten compound which is aggressively corrosive. It will eat away most heat resistant alloys in less than a year.

A high level of sulphur in the oil might be 2 or 3%, while only 0.05% (or, 500 parts per million) of vanadium is “high” enough to be destructive. Venezuelan oil is particularly high in vanadium and is often used in the Northeastern U.S.A.

The alloys with good resistance to fuel ash corrosion are usually cast compositions that are both weak and brittle. 50Cr-50Ni cast IN-657 (UNS R20501) is the best, while HE (28Cr 9.5Ni) is said to be reasonable. IN-657 is expensive and readily embrittled, and HE is particularly weak and brittle.

Available wrought alloys are not at all as resistant to fuel ash corrosion but are used for their much better ductility. RA333, RA625, RA330, RA 253 MA and RA310 have all been used or are on trial. Frankly, we have no good comparative field data for these wrought alloys. Mostly based on rumor, we might suggest RA333 or RA 253 MA as worth trying, but they definitely will not be as good as 50%Cr-50%Ni cast.