High Temperature Alloy Corrosion by Halogens

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Difficulties of alloy selection for high-temperature halogen service are described with reference to product morphologies, vaporization and the manner by which alloy degradation may occur. Selected results from work with alloy 600 (Ni-16 Cr-8Fe) and Haynes® Alloy 230 (Ni-22 Cr-14W-2Mo-0.3Al-0.02 La) are used to contrast various modes of attack. Oxidizing chlorine-containing gases often give rise to heavy volatilization and intergranular attack at 900°C (1650°F) whilst HF/steam mixtures result in more uniform internal oxidation at 750°C (1380°F).

INTRODUCTION

Alloy performance at high temperatures is hindered by scale vaporization and adhesion loss from unstable reaction products and highly mobile halogen species. This area of study is difficult, and data, where available, may be unreliable or unrealistic because process conditions are rarely reproduced in the laboratory. Of particular concern are processes involving halogens where temperatures often exceed 500°C (930°F) and where other oxidant species (such as air, steam or sulphur) may also be present. Figure 1 highlights some representative applications and further indicates the complexity of several environments where conditions may not always remain oxidizing.

The possibility of simultaneous scale growth and evaporation is prominent in considering metal-halogen gas reactions.[1-2] Representative thermodynamic data (Figure 2) indicates the relative instability of metal chlorides compared with oxides and fluorides. Halide vapor pressures of common base metals (Ni, Co, Fe) and scale forming elements (Al, Cr) can also be significant ($>10^{-4}$ atm.) as temperatures exceed 550-600°C (1020-1110°F)[1]: Table I provides representative data and includes the melting points of oxides for comparative purposes.

Fluorides tend to be more stable than chlorides, but each species has significant solubility and diffusivity in metals at high temperatures.[3-4] Zones of internal chloridation have been noted for dilute Ni-Cr alloys (Ni-2 at % Cr) exposed for 2-4 days at 700-900°C (1290-1650°F)[3] and for various commercial alloys exposed to air –2% Cl_2 for 50h at 900°C (1650°F).[2,5-6] Internal fluoridation has been reported for Ni-5.6% Cr exposed at 800-950°C (1470-1740°F) in a fluoridation atmosphere.[4] Internal precipitates were identified as chromium fluoride. In work with HF at 650°C (1200°F), a series of nickel-base commercial alloys exposed for times up to 100h exhibited a similar predominance of internal fluoridation.[7-8]

Grain boundary effects present after exposure to chlorine-containing atmospheres[3] are also significant in work reported for alloy exposure at 900°C (1650°F) in air –2% Cl_2.[5,9] In some cases, significant intergranular attack was observed even after 50h exposure at 900°C (1650°F). Reducing conditions at 900°C (1650°F) (e.g. Ar-HCl-H_2 mixtures), by contrast to oxidizing mixtures, tend to show less dramatic wastage for a range of commercial alloys.[9] Damage remained significant with respect to voidage within alloy-affected zones, aluminum-containing alloys proved to be attractive, as were 'acid-resisting' alloys such as C-276 (Ni-16Cr-5Fe-16Mo-4W-0.08Si-1.0Mn). However, this latter alloy pitted and corroded badly on exposure to more oxidizing conditions[5,9] for similar times and temperatures.

Internal voids within the alloy-affected zone are a regular feature of cross-sectional metallography for oxidizing environments. The rationalization of this phenomenon is biased towards a mechanism in which the generation of volatile halides provides a rapid means for transporting metal ions away from the metal. The outward migration of ions will be balanced by a counterflow of vacancies which condense out, probably as an accumulation of voids. Those voids which coalesce at or near the metal surface may result in a reduced contact area with attendant diminution in the adhesive strength of a 'normal' oxide.

Less volatility is anticipated in fluorine-containing atmospheres (Table 1), and the extent of internal voidage may not be so extensive. High nickel alloys provide the most useful resistance to F and HF[7,10] due to formation of an outer, highly protective fluoride film. The slow growing NiF_2 product is resistant to volatilization at 800°C (1470°F).[1] Alloying elements such as Al, Ti, Cr, Mn and Fe are highly reactive towards fluorine-containing gases. However, the high solubility/diffusivity product (NxDx) for F in nickel is five times that for O in nickel, and twice that for Cl in nickel at 750°C (1380°F).[3-4] This ensures that fluoridation proceeds internally with less external scale growth.
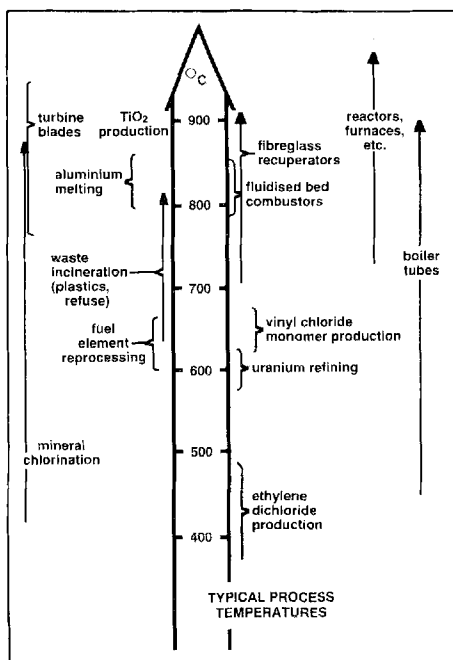

Figure 1. Representative temperatures in commercial processes.

Exposure to oxidizing fluorine atmospheres (e.g. HF-steam) introduces some oxide products but morphologies are not too dissimilar from those noted for exposure to anhydrous HF.[7]

EXPERIMENTAL

Tests have been conducted in various flowing gaseous environments as part of on-going studies.[6, 12-13] Chlorine reactions were carried out for 50h periods at 900/1000°C (1650/1830°F) in an 'oxidizing' (air –2% Cl_2) or 'reducing' (Ar-25% H_2-10% HCl-5% CO-1% CO_2) environment. These provided partial pressures of ~2×10^{-1} atm. pO_2/2×10^{-2} atm pCl_2 and 5×10^{-20} atm pO_2/5×10^{-11} atm ρCl_2 respectively at 900°C (1650°F).[14] Fluorine reactions were carried out for 150h periods at 650 to 850°C (1200 to 1560°F) in an 'oxidizing' (HF-steam) environment, with partial pressures of 2.7×10^{-8} atm pO_2 and 9×10^{-17} atm. pF_2 respectively at 650°C (1200°F).[7]

Halogenation experiments were performed in horizontal silica reaction tubes (chloridizing environments) or alumina tubes (fluoridizing environments), using triplicate samples ($1.5 \times 0.5 \times 0.1$ cm) of the same candidate material to avoid cross-contamination effects. Gas flows were typically 20-30 cm^3/min through 2.5 cm bore reaction tubes. The pressure was close to atmospheric.

Chlorine gas mixtures, supplied in high pressure cylinders, were dried through and over concentrated sulfuric acid (as needed) at ambient temperature and metered using a simple rotameter. Hydrogen fluoride was delivered from low pressure liquified gas cylinders, distilled off from the liquid phase and metered using a 'mass-flow meter' device. Steam was injected using a 'flash-boiler' technique. Halogen off-gases were passed/pulled through dilute caustic scrubbers to remove unreacted halogen vapors.

Samples were prepared for conventional optical and electronoptical analysis recognizing the difficulties of handling scales that may be detached from their substrates with further complications from hygroscopic tendencies. Chlorides can be very reactive on occasion[2] unlike fluorides which have relatively lower water solubility.

## RESULTS AND DISCUSSION

Chlorine-Containing Environments

The relative potentials of chlorine and oxygen have significance on material performance, as demonstrated in the cross-sectional micrographs in Figure 3. The intergranular features are typical of nickel-base alloy performance after 50h exposure at 900°C (1650°F) to air-low% chlorine gases. The Alloy 230 samples exhibited voids and deep intergranular attack for the air-2% Cl_2 situation (Figure 3(a)) with about 20% less damage in the more reducing argon-HCl-H_2 gas (Figure 3 (b)). Similar tendencies were noted in other reports for Ni-Cr-W/Mo-rich alloys such as Hastelloys (Ni-15.5Cr-14.5Mo-0.02La)[15] and the similar Hastelloy alloy C-276.[9] Environments richer in oxygen tend to favor the development of fast-growing oxides (iron-, nickel- or cobalt-) that overgrow the 'barrier' sublayers based primarily upon chromia and/or alumina. Evidence favors direct conversion of metal oxide to vaporous halide with subsequent enhanced formation of volatile products. For example:

$$NiO_{(s)} + Cl_{2(g)} \rightarrow NiCl_{2(g)} + 1/2\ O_{2(g)}$$
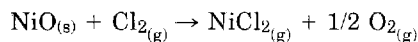
Such volatile products tend to migrate outwards, away from the metal, until they reach zones of higher oxygen potential, where displacement reactions may then be favored. For example, the reaction involving metal (M) may be represented:

$$2M\ Cl_{2(g)} + O_{2(g)} \rightarrow 2\ MO_{(s)} + 2\ Cl_{2(g)}$$
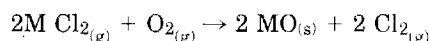
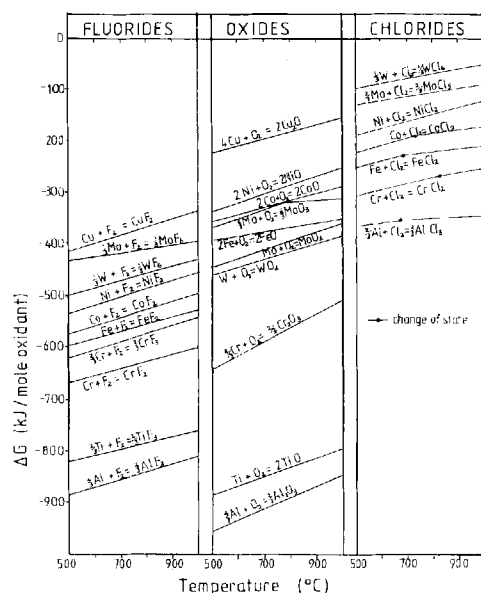Thus, more halogen can be made available for reaction or release to the

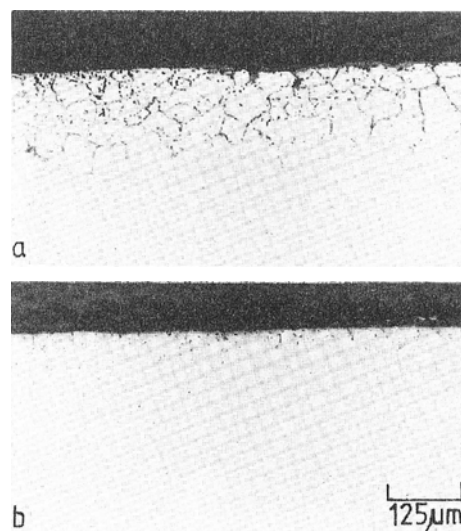Figure 2. Selected thermodynamic data for fluorides, chlorides and oxides.

Figure 3. Cross-sections for H.230 after 50h at 900°C. (a) In air 2% Cl_2. (b) In argon 25% H_2 10% HCl 5% CO 1% CO_2.

Table I. Summary of m.p. and v.p. Data

	Fluorides		Chlorides		Oxides	
	mp	Tv	mp	Tv		mp
FeX_2	1020	906	676	536	FeO	1378
FeX_3	1027	673	303	167	Fe_2O_3	1594
NiX_2	1450	939	1030	607	NiO	1955
CoX_2	1250	962	740	587	CoO	1805
CrX_2	894	(928)	820	741		
CrX_3	1404	855	1150	611	Cr_2O_3	2400
AlX_3	>1273	825	193	76	Al_2O_3	2050

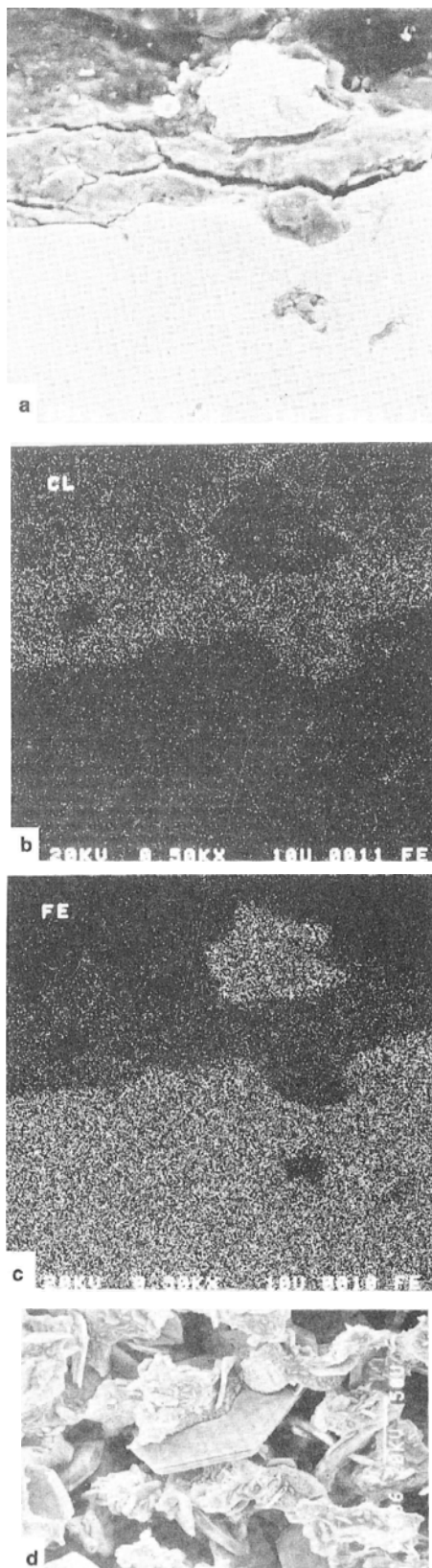mp = melting point (°C).   Tv temperature (°C) at which the halide v.p. is 10^{-4} atm.

Figure 4. Attack on pure iron in argon 25% H_2 10% HCl 5% CO 1% CO_2 after 50h at 900°C. (a)-(c) Electron, chlorine-and iron-X-ray maps. (d) Surface morphology by SEM.

environment. This rapid migration of species often results in voids within the alloy matrix, but the presence of carbides may also be contributory. Work elsewhere has associated voids with the dissociation of chromium-rich particles (e.g. carbides).[16] Carbon, released from the precipitated phase may form new carbides adjacent to the original locations (e.g. grain boundaries). Chlorides have also been noted in grain boundary regions following exposure of Co-Cr alloys to molten salts at 900°C (1650°F).[17]

The more 'reducing' type of environment tends to be less aggressive because chromia-and alumina-scale layers form preferentially. Oxides of iron-, nickel- and cobalt are less stable at lower oxygen potentials, reducing the tendency for extensive scale formation that is noted in the more 'oxidizing' conditions. In the absence of the Cr- or Al-rich layers, when protective scales cannot form, there is substantially more attack. Figure 4 shows the extent of attack on pure iron exposed for 50h at 900°C (1650°F) in Ar-25%H_2-10%HCl-5%CO-1%CO_2. Electronmicroscopy reveals chloride-rich cracked scales that are far more complex compared with oxide-scales on similar material.

Iron oxides are known to be unstable in HCl environments,[18-19] yielding volatile compounds at the exposure temperatures typified by the present studies. Catastrophic oxidation has been reported for iron exposed to HCl/O_2 at 700°C (1290°F) due to the formation of low melting point volatile $FeCl_3$ and steam due to oxychlorination.[20] Other workers,[21] have observed increased corrosion rates on boiler steels exposed to flue gases containing HCl at 540-1000°C (1005-1830°F). Hydrogen chloride rendered scales more porous and less continuous.

Fluorine-Containing Environments

Figure 5 clearly demonstrates that internal fluoridation characterizes alloy attack after exposure to fluorine-containing atmospheres. This shows a representative cross-section of nickel-base alloy 600 (Ni-16 Cr-8 Fe) after 150h exposure to HF/steam at 750°C (1380°F). The corrosion process involves the formation of internal chromium-and iron-rich fluorides at an advancing reaction front within the nickel-rich matrix (Figures 5 (b) - (d)).

Fluoridation reactions are usually characterized by the very uniform nature of the reaction front (Figure 5 (a)) and by its rapid inward growth.[7,8,10,12] In many systems, individual precipitates persist for long periods (e.g. > 150h at 750°C (1380°F) to HF before linking-up to produce 'layers'. These fluoride 'layers' are not of a 'healing' nature and inward diffusion of fluorine atoms usually continues unimpeded.

Volatilization is anticipated for NiF_2 and CrF_3 above 800°C (1470°F), although at low gas flow rates these losses may be small. In complete contrast to the corresponding chlorides of their elements (c.f. Figure 4), iron- and aluminum-fluorides are generally more volatilization-resistant. Compared with chlorine-containing environments, volatilization is typically less of a problem in fluorine environments. One limitation may arise with Mo-containing alloys, where the susceptibility to volatiles may be significant because MoF_6 melts at 17°C (65°F).

The choice of materials for halogen service will also be dictated by adequate mechanical properties and thermal stability. Commercial purity nickel (Ni 200) and MONEL®400 have excellent resistance to F and HF at elevated temperatures,[1,7] but they have serious mechanical limitations. Precipitation-strengthened, high performance alloys exist[15] but may be prone to limitations of intergranular corrosion (c.f. chlorides). The volume fraction of internal precipitates is tending to increase with the advent of the 'stronger' superalloys. This may introduce risks of cracking especially where mechanically weak precipitates link-up to produce a continuous fluoride layer within the alloy matrix. Both chlorine and fluorine may be important in grain boundary embrittlement phenomena[3,16]

CONCLUSIONS

Halogens are readily soluble and diffuse rapidly into metals at high-temperature and can cause problems in high-temperature corrosion. The solubility-diffusivity product (NxDx) for F in nickel is about 5 times that for O in nickel and about 2 times that for Cl in nickel at 750°C (1380°F).

Oxidizing-chlorine environments (e.g. air-2% Cl_2) are more damaging at 900°C (1650°F) than 'reducing' environments (e.g. Ar-25% H_2-10% HCl-5% CO-1% CO_2. Alumina-forming alloys are often the best choice overall but acid-resistant alloys, rich in Cr and refractory metal, show reasonable performance to the 'reducing' atmospheres, unlike pure iron, for example.

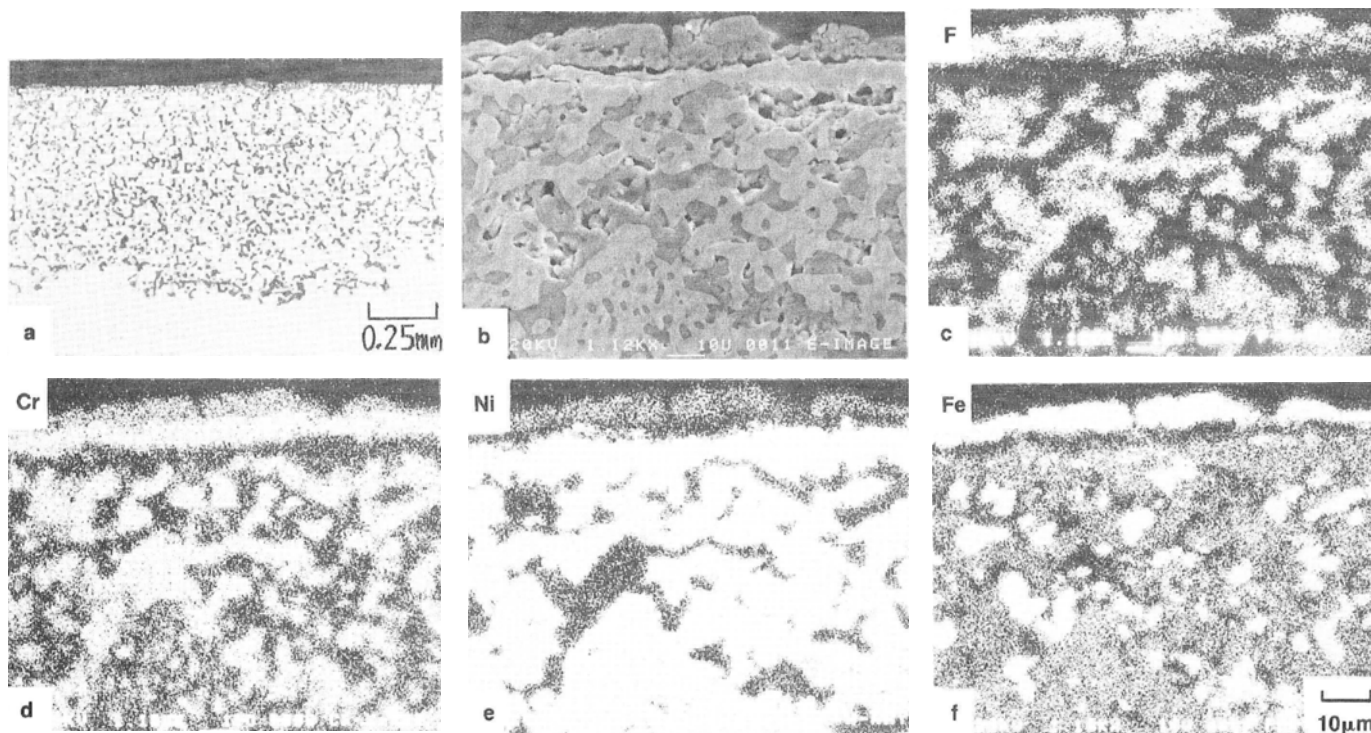Chlorine attack is often associated with internal voidage and intergranular attack.

Figure 5. Cross-sections for Alloy 600 after 150h at 750°C in HF/steam. (a) Optical view of internal CrF$_2$ precipitates. (b) SEM detail of (a) electron image. (c) F X-ray map. (d) Cr X-ray map. (e) Ni X-ray map. (f) Fe X-ray map.

Fluorine corrosion is usually by internal fluoridation with the formation of a uniform reaction front. Volatilization is less of a problem with fluorine-compared with chlorine-containing environments.

ACKNOWLEDGEMENTS

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