A practical guide to high-temperature alloys

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Abstract

The requirement for materials which can operate at ever-higher service temperatures continues. Corrosion problems are a limiting factor and have been countered by improvements in material compositions, coating procedures and fabrication techniques. Existing high-temperature alloys are reviewed, leading to a discussion of their performance in a variety of corrosion environments – oxidation, sulfidation, hot corrosion, fuel ash corrosion, carburisation and halogen attack are considered. Options are given for each environment but it is emphasised that material selection cannot be separated from consideration of other factors of the high-temperature system, including process control and better overall design specifications.

High-temperature materials are used for many critical components in a wide number of industries, including power generation, chemical processing and gas turbine. With continuing demands for increased throughput and efficiency, there has been a trend towards higher service temperatures and pressures. This has resulted in continued corrosion problems, countered by continued improvements in material compositions (such as minimizing detrimental trace elements), coating procedures, and improved fabrication, notably casting, forging and welding. For example, in the gas turbine industry, alloys designed to cope with high-stress-bearing/elevated temperature scaling are now used for service temperatures in excess of 1100°C, compared with about 800°C some 40 years ago.

All materials have their limitations and the solution to high-temperature problems is often a compromise between careful material selection (when a cause is known), process control (to impose a safe limit for temperature or gas composition, *etc*), and better design specifications (to recognise mechanical constraints at elevated temperature or resulting from thermal cycling). The ultimate choice will be a compromise based on what is available and how much it costs. In some cases it is rational to accept a short life expectancy with a high reliability factor where the component is replaced on a planned-time schedule.

Effect of temperature

High temperatures acccelerate corrosion processes. The result is that certain gases or liquids, which are considered innocuous under ambient conditions, become aggressive to materials when hot. A ten-fold change in corrosion rate is not uncommon for a temperature change of 30°C under aqueous corrosion conditions. The same ten-fold change (or considerably worse) can occur with a 20°C change under high-temperature oxidation conditions.

Most common process temperatures are in the range 450° to 850°C or higher (Figure 1). Materials of construction must withstand excessive metal loss by

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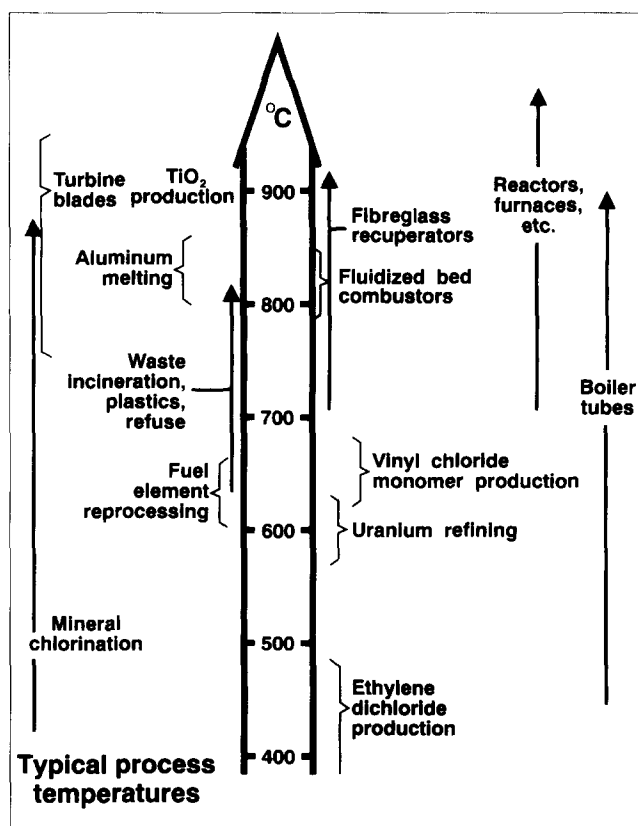
Fig 1   Representative process temperatures

scale formation from oxidation and from penetration by internal oxidation products that could reduce the remaining cross-sectional area to a level that cannot sustain the load-bearing requirements. The component will then yield and may swell or distort. In some cases the internal fluid pressures can be sufficient to burst the component releasing hot, possibly toxic or flammable fluids. Heating and cooling rates can also be significant because of possible thermal stress (fatigue) effects.

Figure 2 shows two examples of failure where mechanical overload is synonymous with the high-temperature failure. In one case, an alloy steel has burst
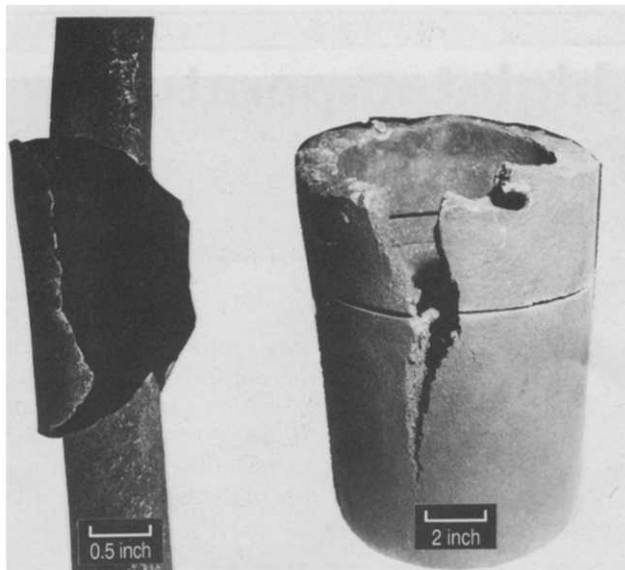
Fig 2   Examples of failure involving mechanical overload: burst tube caused by overheating (left); rupture of reformer tube following repeated uncontrolled thermal cycles (right)

from overheating. In the second case, a reformer tube, the cracking results from a combination of the corrosion processes (involving carbon) and the effects of repeated thermal cycling.

Oxidation and scaling

Most high-temperature reactions involve oxidation processes. In part this is because oxides are common products of reaction in the many applications where air or oxygen-rich environments pertain. Oxidation in clean, non-polluted gases (air, oxygen) results in the formation of a thin oxide film that develops into a thicker scale. The scale formation is controlled by thermodynamic and kinetic factors, notably gas composition and temperature. The "scaling" temperature for carbon steel is
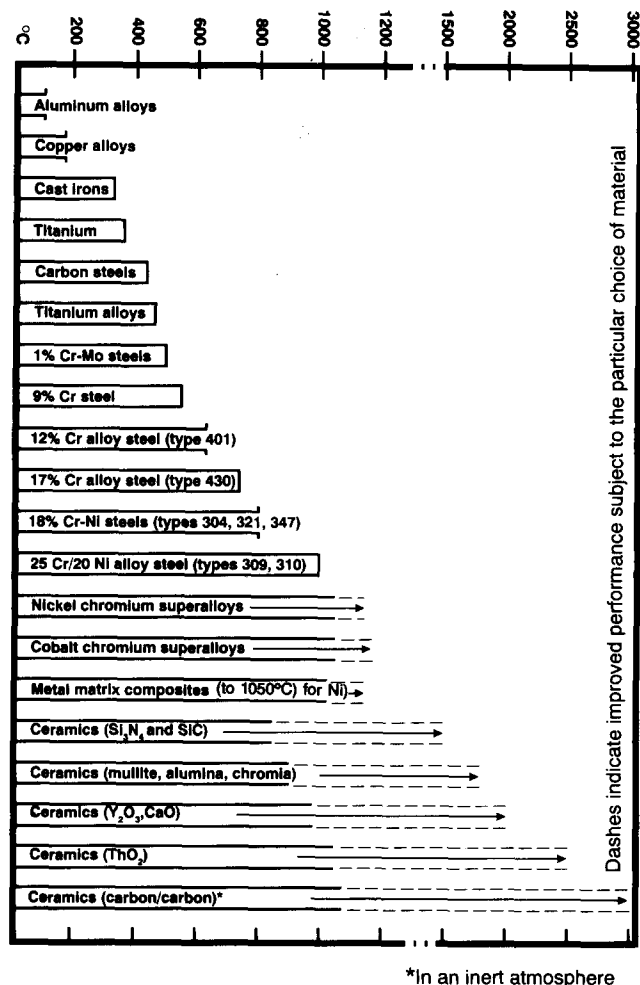

*In an inert atmosphere

Fig 4   Maximum service temperatures of common engineering materials suggested for isothermal oxidation in clean air or oxygen

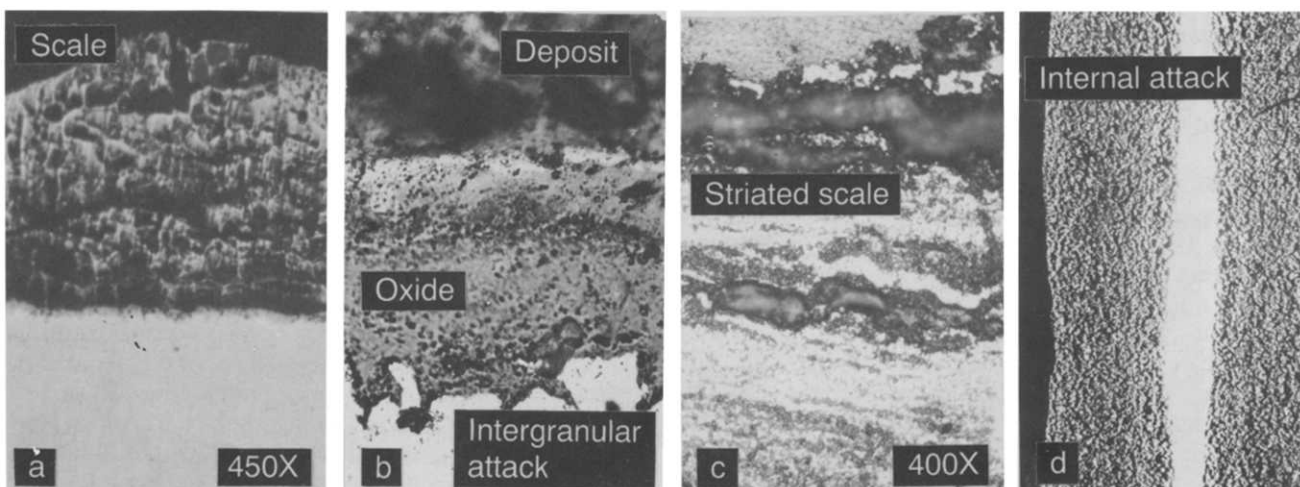about 550°C, wich reflects the temperature where iron produces wustite (FeO).

Fig 3   Influence of environment on alloy/scale morphology: (a) porous, cracked oxide scale; (b) deposit/scale with intergranular corrosion in boiler superheater tube; (c) stratified scale from recuperator where fused salts were present; and (d) gross internal fluoridation with oxidation. (Photo: C J Tyreman)

Table 1   High-temperatue alloys   – Nominal compositions (wt %)

Alloy	UNS No.	Fe	Ni	Co	Cr	Mo	W	Al	Si	C	Other
9Cr-1Mo	S50400	bal			9	1			0.5	0.12	
Type 304	S30400	bal	9		19				0.75	0.08	
Type 316	S31600	bal	11		17	2			0.75	0.08	
Type 317	S31700	bal	12		18	3			0.75	0.08	
Type 309	S30900	bal	13		25				0.5	0.15	
Type 310	S31000	bal	20		25				0.5	0.15	
Type 321	S32100	bal	10		18				0.5	0.05	0.4 Ti
Type 347	S34700	bal	11		18				0.5	0.05	0.04 Nb
Type 410	S41000	bal			12					0.1	
Type 430	S43000	bal			17				0.4	0.10	
Type 446	S44600	bal			25				0.8	0.20	
E-Brite* (XM-27)	S44627	bal			26	1				0.01	0.1 Nb
RA* 85H		bal	14.5		18.5			1.0	3.5	0.20	
Type HH	J93503	bal	12		25				1.4	0.40	
Type HK	J94224	bal	20		25				1.5	0.40	
Type HP		bal	35		25				1.5	0.4	1.5 Nb
Type HT	J94605	bal	34		17				1.2	0.40	
IN-519		bal	24		24				1.5	0.35	1.5 Nb
RA* 330	N08330	bal	34		19				1.2	0.05	
Fecralloy*		bal			16			4.7		0.02	0.3 Y
Incoloy* DS		bal	37		18				2.20	0.03	
Alloy 800	N08800	bal	32		21			0.2	0.4	0.04	0.4 Ti
Alloy 800H	N08810	bal	32		21			0.2	0.4	0.10	0.4 Ti
Haynes* 556	R30556	bal	20	18	22	3	2.5	0.2	0.4	0.10	0.6 Ta, 0.02 La
Multimet*	R30155	bal	20	20	21	3	2.5		1.0	0.08	1.0 Nb/Ta
Alloy 718	N07718	18.5	bal	1	19	3		0.5	0.35	0.08	5.1 Nb/Ta, 1 Ti
Alloy 600	N06600	8	bal		16				0.3	0.06	
Alloy 601	N06601	14	bal		22			1.4	0.2	0.03	0.2 Ti
Nimonic* 75	N06075	2.5	bal		19.5					0.12	0.4 Ti
Nimonic* 80A	N07080	1.5	bal	1	19.5			1.4		0.05	2.25 Ti
Nimonic* 90	N07090	1.5	bal	17	19.5			1.4		0.06	2.4 Ti
Nimonic* 105			bal	20	15	5		4.7		0.08	1.2 Ti
Inconel* 617	N06617		bal	12	22	9		1.2	0.2	0.07	0.4 Ti
Alloy IN-657	N07765	bal			50					0.03	1.5 Nb
Inconel* 690	N06690	9	bal		29				0.4	0.03	
Haynes* 214		3	bal		16			4.5	0.1	0.03	0.02 Y
INC MA 754*			bal		20			0.3		0.05	0.6 Y_2O_3, 0.5 Ti
INC MA 956*		bal			20			4.5			0.5 Y_2O_3, 0.5 Ti
Haynes* 230	N02230	3	bal	5	22	2	14	0.3	0.4	0.10	0.02 La
RA* 333	N06333	18	bal	3	25	3	3		1.25	0.05	
Alloy R-41	N07041	5	bal	10	18	9		1.5	0.5	0.08	3 Ti
Alloy 263	N07263	1	bal	20	20	6		0.5	0.4	0.06	2 Ti
Haynes* HR-160		4	bal	27	28				2.75	0.05	
Alloy 625	N06625	3	bal		22	9		0.2	0.2	0.02	3-5Nb/Ta, 0.3 Ti
Hastelloy* N	N10003	5	bal		7	17			1.0	0.06	0.3 Cu
Hastelloy* S	N06635	2	bal	1	16	14	0.8	0.2	0.5	0.02	0.05 La
Alloy X	N06002	18	bal	2	22	9	0.5	0.2	0.5	0.15	0.15 Ti
Waspalloy*	N07001	2	bal	14	19	4		1.5		0.08	3 Ti
Alloy 25 (L605)	R30605	2	10	bal	20		15		0.4	0.1	
Alloy 150		18	1	bal	27				0.3	0.06	
Alloy 188	R30188	2	22	bal	22		14		0.4	0.10	0.04 La
Alloy 6B		3	3	bal	30	1.5	4.5		2.0	1.2	

*Trademark

Wustite contains many ionic defects that permit rapid transport of reactant species and hence more extensive scaling with associated metal wastage. Ideally, a scale should be continuous, adherent, stoichiometric and coherent. This will effectively reduce the rate of oxidation. If the scale is porous or noncontinuous, or if it contains other chemical species, notably sulfur or chlorine, then further corrosion will occur, often at an accelerating rate. Different morphologies result from various service environments, noted from the representative cross sections in Figure 3. In some cases there may be excessive scaling; in other cases there may be predominant internal oxidation.

Maximum service temperatures of common engineering materials in clean air or oxygen are indicated in Figure 4. These can only serve as guidelines. These temperatures are decreased when the atmosphere contains pollutants or when liquid metals or molten salts are present. Service temperatures are further reduced when components are under stress or if they experience repeated thermal cycling. Intergranular corrosion processes can be instrumental in early failure.

Materials

Candidate materials for high-temperature service need to be strong and resistant to oxidation or other corrosion processes. Alloy steels and more sophisticated alloys based on nickel or cobalt are most commonly used. Ceramic materials are finding more applications for temperatures above 870°C. There are durability and handling problems but applications thus far have been beneficial for recuperators and heat exchangers. Most of these materials are based on silicon carbide, silicon nitride, or other oxide ceramics. High-temperature corrosion data for ceramics are not always available. Performance will in part be related to the silica-containing oxidation products.

Various composite materials are now available for specific high-temperature applications, often where

strength is a primary target. These include dispersion-strengthened alloys for aerospace applications. Common examples are yttrium oxide dispersed in nickel alloys and alumina in aluminium alloys. These materials are effectively produced by mechanical alloying techniques.

Intermetallic compounds are mostly intermediate between conventional metallic alloys and ceramics. These materials have very high yield stresses. Typical intermetallics include Ni_3Al, $NiAl$, Ti_3Al and Ni_3Si. Aluminium and silicon each contribute to the formation of adherent oxide scales at elevated temperatures. These materials are of special interest to the aerospace industries but also find applications elsewhere. For example, nickel silicide has excellent resistance to hot sulfuric acid.

Table 1 is a representative listing of some high-temperature alloys. Chromium is a key element for oxidation resistance provided temperatures do not exceed 950°C for long periods of time. Under these conditions, chromium may vaporise and liberate CrO_3 instead of forming the more desirable barrier oxide scale rich in chromia (Cr_2O_3) or spinel ($M_2Cr_2O_4$). Chromium is not recommended for fluorine-containing gases at high temperatures.

Aluminium provides excellent oxidation resistance by forming aluminium-oxide scales. These are thermodynamically more stable than chromium oxide and are less prone to vaporisation effects. When chromium and aluminium are each present within an alloy, they will compete to form a surface scale. For some alloy composition ranges – for example, with 5% aluminium and about 5% chromium – alumina develops in preference to chromia. These "alumina-forming" (or aluminium-containing) alloys provide useful resistance to halogen vapours and sulfurous gases [for example, alloy 601 (UNS N06601) and Haynes[+]214].

Silicon, like aluminium, acts conjointly with chromium to improve scale resilience in aggressive environments. Silica-containing oxides act like "glazes" and alloys that contain up to about 2.5 to 3.5% Si (for example, alloys RA 85H and HR 160) are finding useful applications in carburising and sulfidising environments.

Rare earth elements, typified by yttrium, cerium, and lanthanum, improve scale adhesion at high temperatures. Surface scales are more resistant to spalling on thermal cycling, and oxidation rates are reduced. Alloys include the iron-chromium-aluminium-yttrium alloy Fecralloy (iron with 16% chromium, 4.7% aluminium, and 0.3% yttrium); Haynes 556 [iron with 22% chromium, 20% nickel, 18% cobalt, 3% molybdenum, 3% tungsten, 0.02% lanthanum (UNS R30556)]; and alloy 214 (nickel with 16% chromium, 4.5% aluminium, 0.03% yttrium). The rare-earth presence assists the development of a more resilient scale, which delays oxidation and other high-temperature corrosion processes, such as sulfidation.

Thermal history, notably the extent of thermal cycling, is critical to material performance. Corrosive environments may lead to degradation that introduces metallurgical changes, rendering a material weak at room temperature, such as sigma formation. Fabrication processing is very important, and this is cited in many manufacturers' literature and specifications. Weld failures can occur because of thermal stresses, poor design or poor practices.

Adequate gaps in assemblies should be left to accommodate the relatively high thermal expansion of some alloys. High nickel contents help to lower the coefficients of thermal expansion, recognising that alloy steels expand and contract much more than simple carbon steels.

Alloy steels

Cast or wrought alloy steels are widely used in the range 800 to 950°C. Cast heat-resistant HH/HK alloys (for example, HK-40, 25% chromium, 20% nickel, 0.40% carbon, balance iron) and the later 25/35/Nb alloys (for example, HP, IN 519) are used for furnace tube applications, particularly in reformer plants. The iron-nickel-chromium alloys are a common choice for many high-temperature applications due to their relatively low cost, good mechanical properties, and moderate oxidation resistance.

Martensitic-type steels containing 12 to 14% chromium show good scaling resistance to about 700°C. However, steels such as type 410 [12% chromium, 0.1% carbon, balance iron (UNS S41000)] can experience embrittlement when tempered, or slowly cooled, in the range 370 to 600°C.

Most high-temperature materials exhibit metallurgical changes following long-term use. In some cases, there is local grain boundary melting ("burning") as a result of gross overheating. In other cases, phases form at the expense of other elements, such as the loss of chromium by carbide formation during sensitisation of austentic steels in the range 510 to 788°C, which renders the steel less resistant to aqueous corrosion.

Sustained heating of ferritic or *cast* austenitic stainless steels between 650 and 870°C can lead to carbide precipitation and sigma- or chi-phase formation, should ferrite-rich areas be present in the casting. Both carbides and sigma or chi phases result in a loss of ductility. Sigma phase (FeCr) is a problem for ferritic steels. This hard, brittle phase forms when a steel is slowly heated in the range 500 to 1000°C. The process is slow in iron-chromium alloys, faster in iron-chromium-nickel alloys and much faster in iron-chromium-silicon alloys. Ferrite-forming elements (silicon, niobium, molybdenum and tungsten) induce sigma unless sufficient nickel is present to stabilise the austenitic matrix.

The type 300 series austenitic stainless steels contain at least 12% nickel. Alloys, typified by types 309 [25% chromium, 13% nickel (UNS S30900)], and 310 [25% chromium, 20% nickel (UNS S31000)] are widely used for good creep strength and ductility in addition to scaling resistance at high temperatures.

Type 310 alloy, with more nickel content, is less susceptible to sigma formation, although all cast materials are likely to contain local ferritic zones that will be sensitive to sigma transformation if service temperatures and times permit. If components operate *above* 870°C continuously, there is little risk of embrittlement. For temperatures of 650 to 870°C, alloy compositions are more critical. Fully annealed, wrought alloys are preferred.

Table 2 Relative material costs

Materials	Relative Cost
Type 310 stainless steel	1
Alloys 800H, RA 330	1.5
Alloys 600, 601	2–3
Alloys 617, 625	2.5–3
Alloy RA 333	3–4
Alloy X	4
Alloy 214	4–5
Alloys 230, 556	6–7
Alloy 188	10–12

Alloys richer in nickel, for example, alloy 800/800H [20% chromium, 32% nickel, balance iron (UNS N08800/N08810)] represent a sensible option for many high-temperature applications. Sigma may still be a problem for some nickel-based alloys, at about 770 to 927°C.

Heat-resistant alloys

Many advanced alloys were developed to meet specific demands, usually involving not only corrosion resistance but also superior strength with fabricability. Alloys developed for service at higher temperatures, or for more aggressive environments, include the superalloys based on the basic binary systems of iron – 20% chromium, nickel – 20% chromium, or cobalt – 30% chromium. They embrace alloys such as the Hastelloys, Incoloys, Inconels, Nimonics and Waspalloy. Some alloys contain up to 50% chromium, as in alloy IN-657 (nickel with 50% chromium, 1.5% niobium). In some cases composite systems are used, for example, as in alloy 800 clad with IN-657.

Various alloying elements play different roles. Some improve strength [solid solution or precipitation hardening; carbide or nitride formers; intermetallics like γ', $Ni_3(TiAl)$]. Other elements improve oxidation or hot corrosion resistance (primarily chromium, aluminium and silicon with endorsement by rare earths). Sometimes the strengthening elements can be lost by environmental reactions. Examples include catastrophic oxidation of molybdenum above about 750°C, enhanced oxidation when vanadium is present, loss of tungsten and molybdenum by halogen vapours, and loss of nickel by low-melting sulfides. These aspects endorse the need to fully appraise systems on a case-by-case basis.

Coatings

Metallic coatings, rich in chromium, aluminium, or silicon, are widely used in high-temperature service environments. The latter two offer resistance to carburising and sulfidising. Silicon has shown some promise in resisting molten vanadium slags.

Costs

Relative material costs are given in Table 2. Costs of highly alloyed materials appear high, but should be balanced against lost time and increased maintenance.

Special corrosion problems

Various types of corrosion can be anticipated from different industrial processes, shown in Table 3.[1-4] Of importance is the possible combination of processes.

Moisture may often be present, and condensation in cooler parts of the plant may also contribute.

If process flue gases contain sulfurous species, notably SO_2 and SO_3, for example in the environment from fuel combustion in boilers, then damage can be heavy as a result of sulfurous and sulfuric acid condensation. Desulfurisation represents one approach to the problem, but keeping temperatures away from susceptible dewpoint levels is another.

Some environments are too complex to permit analysis. Some processes are unpredictable. On-site screening is warranted with laboratory support to better define the rate-controlling parameters. Corrosion parameters are not as well established for high temperatures as they are for aqueous corrosion.

Other critical factors are flow patterns and erosion, particulates and deposit formation, and the possibility of liquid phases including liquid metals or fused salts. Other factors include heating type, flame impingement, hot flue gases, molten metals or fused salts, and friction or wear.

Oxidation

When an alloy is heated above the maximum service temperature (Figure 4), heavy scale can form. Overheating accounts for most service problems, which become severe as temperatures exceed 1100°C, with the high-alloyed materials. Most high-temperature alloys can be used generally up to 1000°C without serious oxidation attack, if gases are clean.

Early failures can be expected when materials are misused, including the common mix-up of carbon steel for an alloyed variety. Gross metal thinning can result in local deformation and ultimately failure, such as a burst tube (Figure 2). Austenitic stainless steel materials may become magnetic when chromium is lost from the matrix, a useful indication of the severity of attack.

Catastrophic Oxidation

Catastrophic oxidation is a problem for alloys containing molybdenum, typified by types 316 and 317 austenitic stainless steels (UNS S31600 and S31700), with nominal 2 and 3% molybdenum, respectively. Refractory metals, such as molybdenum, tungsten, tantalum, and niobium undergo rapid reactions in oxygen at high temperatures. The oxidation processes occur at accelerating rates, usually with exothermic tendencies (heat evolved). Scales are bulky and under severe compressive stress, since their volume is higher than the atomic volume of the metal on which they form. The final products are often loose and powdery. Figure 5 shows the temperature limitations for molybdenum. There are low-melting, high-vapour pressure oxides. (MoO_3) and eutectics based on metal oxides – MoO_3 and MoO_3-MoO_5. Alkali metal oxides (Na_2O) can limit a material to about 550°C, especially if stagnant conditions prevail.

Fuel combustion – hot corrosion

Combustion products from fossil fuels include complex mixtures of sulfur and oxygen species, alkali metal salts, and halogen vapours or compounds. Flue gases are generally oxidising in nature, but can be reducing (such as sulfidation) on the metal surface, especially when
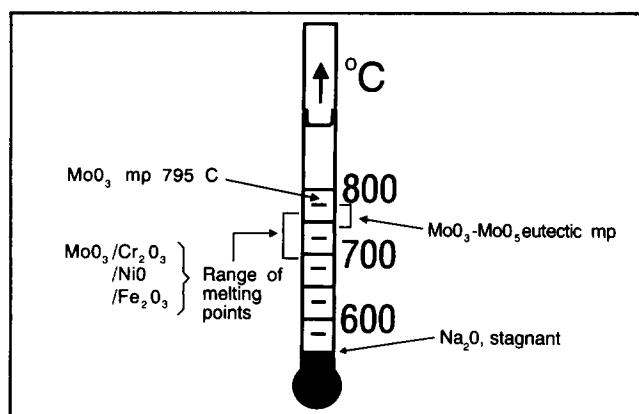
Fig 5 *Temperature limitations that define catastrophic oxidation for molybdenum alone or with other compounds*
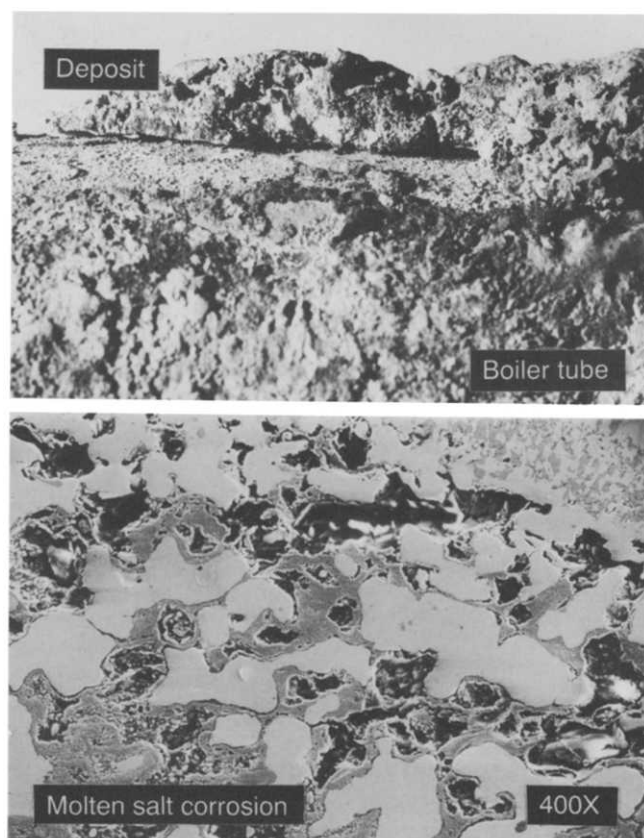

Fig 6 *Boiler tube with deposits. Lower photo shows advanced stage of molten salt corrosion. Liquid phases can be noted*

deposits are also present (Figure 6). Breakaway corrosion can result from low-melting phases.[5, 6]

Clean combustion atmospheres are created on burning natural gas or distillate-grade fuel oil. Highly alloyed materials will generally be adequate for direct contact with the environment (combustion zones, uncooled tube supports, *etc*). In some cases, additional protection is sought from metallic coatings. In boilers, superheater tubes with chromium-molybdenum steels are used provided temperatures are controlled below the point at which molten deposits can form.

Table 3   Representative process conditions (After References 1 and 2)

Process/Components	Temp °C	Type of Corrosion
Chemical/petrochemical		
Ethylene steam cracking furnace tubes	to 1000	carburisation; oxidation
Steam reforming tubes	to 1000	oxidation; carburisation
Vinyl chloride crackers	to 650	halide gas
Hydrocracking heaters, reactors	to 550	H_2S and H_2
Petroleum coke calcining recuperators	816	oxidation; sulfidation
Cat cracking regenerators	to 800	oxidation
Flare stack tips	950-1090	oxidation; thermal fatigue; sulfidation: chlorination. dewpoint
Carbon disulfide furnace tubes	850	sulfidation; carburisation; deposits
Melamine production (urea)-reactors	450-500	nitriding
Other processes		
Ti production reactor vessels	900	oxidation; chlorination
Nitric acid – catalyst grid	930	oxidation; nitriding; sulfidation
Nuclear reprocessing reactors	750-800	oxidation (steam); fluorination (HF)
Oil-fired boiler superheaters	850-900	fuel ash corrosion
Gas turbine blades corrosion	to 950	sulfates, chlorides; oxidation; ash
Waste incinerators – superheaters	480	chlorination; sulfidation; oxidation; molten salts
Fibreglass manufacturing recuperators	1090	oxidation; sulfidation; molten salts

Table 4
Representative kinetic data for 800°C $(mg^2/cm^5/s)$

Material	Oxidation	Sulfidation	Sulfidation/ Oxidation
Nickel	5.6×10^{-5}	$1.6^{(1)}$	2.9×10^4
Nickel – 20% Chromium	1.0×10^{-6}	9.1×10^{-2}	9.1×10^4
Cobalt – 25% Chromium	1.4×10^{-7}	7.5×10^{-2}	5.3×10^5
(1) 650°C			

Sulfidation

Sulfidation, like oxidation, involves the interaction of a metal to form sulfide scale. Kinetics are faster than for oxygen (air) alone, because sulfides are more defective and have lower melting temperatures and less stability, overall, than oxides. Table 4 shows some representative kinetic data.
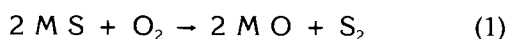
Iron-based alloys are usually the first choice for sulfur-containing environments. The 9 to 12% chromium steels are used for organic sulfides and for hydrogen sulfide. Austenitic types, typified by type 310 (20% nickel, 25% chromium), alloy 800 (32% nickel, 20% chromium), and RA 330 [34% nickel, 19% chromium, 1.5% silicon (UNS N08330)], are often used. Cobalt-containing alloys, such as alloy 6B (low nickel, 30%chromium), and alloys 25 (UNS R30605), 188 (UNS R30188), and 556 (Table 1) are of benefit in aggressive sulfidation conditions. In part, the benefit is attributed to the high iron-iron sulfide eutectic temperature, 988°C. The eutectic temperatures for cobalt and nickel are lower than those for iron (Table 5.).

Table 5 Representative melting points of constituents common to high-temperature environments

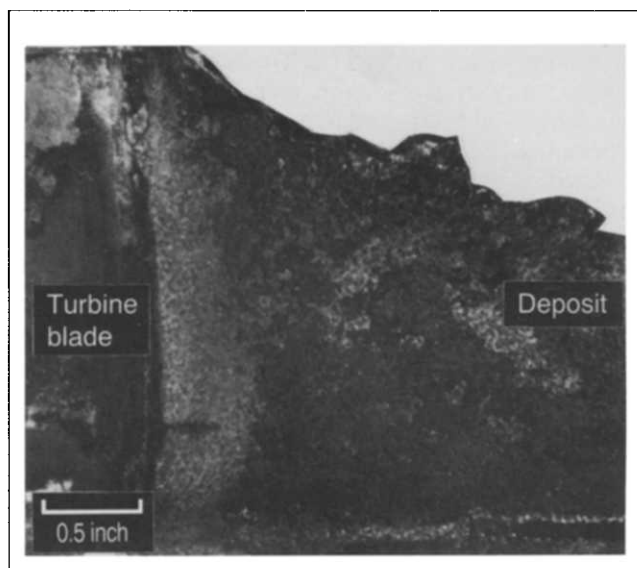| Constituent		Melting point (°C)
$NaVO_3$		630
$CrVO_4$		810
$FeVO_4$		816
MgV_2O_6		700
CoV_2O_6		705
NiV_2O_6		720
V_2O_4		>1750
V_2O_3		690
$Na_2O \cdot V_2O_5$		630
$Na_2O \cdot 3V_2O_5$		621
$2Na_2O \cdot 3V_2O_5$		620
$2Na_2O \cdot V_2O_5$		640
$3Na_2O \cdot V_2O_5$		850
$10Na_2O \cdot 7V_2O_5$		573
$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$		625
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$		535
$2MgO \cdot V_2O_5$		835
$3MgO \cdot V_2O_5$		1190
Na_2O/MoO_3		550
$Ni-Ni_3S_2$		645
FeO-FeS eutectic		940
Fe-FeS eutectic		988
Co-CoS		877
$NaHSO_4$	decomp. $\rightarrow Na_2S_2O_7 + H_2O$	250
$Na_2S_2O_7$		400
$K_2S_2O_7$		335
$3K_2S_2O_7 \cdot Na_2S_2O_7$		280
$Na_3Fe(SO_4)_3$		624
$K_3Fe(SO_4)_3$		618
$Na_3Fe(SO_4)_3 \cdot K_3Fe(SO_4)_3$		552
$Na_3Al(SO_4)_3$		646
$K_3Al(SO_4)_3$		655
$ZnSO_4$	decomp.	740
Na_2SO_4		884
K_2SO_4		1076
$MgSO_4$	decomp.	1124
$Al_2(SO_4)_3$	decomp.	$770 \rightarrow Al_2O_3$
$CaSO_4$		1450
$Fe_2(SO_4)_3$	decomp.	$480 \rightarrow Fe_2O_3$
$NiSO_4$	decomp.	$783 \rightarrow NiO$
$MoCl_5$		194
$NbCl_5$		205
$FeCl_3$		282
Na_2SO_4 –NaCl eutectic		625
NaCl		800
KCl		776
$CaCl_2$		772
$CrCl_2$		820

Fig 7   Hot corrosion damage to a gas turbine blade that shows evidence of a molten sulfate deposit
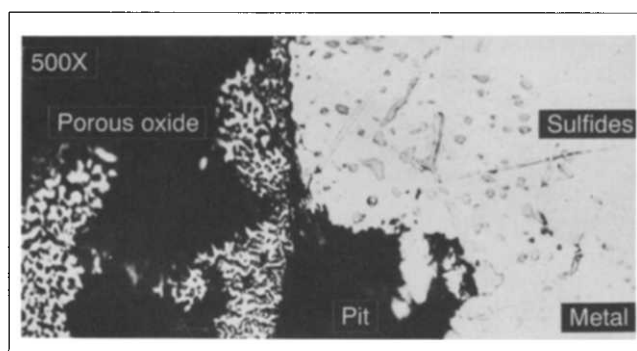

Fig 8   Cross section of nickel-based alloy suffering from hot corrosion by a molten sulfate/chloride. Note the pitted surface and the sulfide penetration into the alloy

Hot corrosion

Hot corrosion is a self-sustaining, accelerating oxidation process. The term was originally used to describe breakaway corrosion in the combined presence of sulfur and oxygen. It now also refers to other processes where low-melting products are present. Displacement reactions occur where, for example, sulfides are converted to more stable oxides. A simplified equation is:

$$2\,M\,S + O_2 \rightarrow 2\,M\,O + S_2 \qquad (1)$$

Sulfur, generated from this reaction, further penetrates the alloy matrix to form more sulfides (where oxygen potentials are low compared with sulfur activity). Such internal sulfides can ultimately react with oxygen to form more oxide and sulfur (as in Equation 1). The sequential progression of oxidation and sulfidation involving the simultaneous presence of the two corrodants is very damaging. Kinetics are enhanced considerably over oxidation or sulfidation alone (Table 4).

Hot corrosion was first encountered in gas turbines (Figures 7) where sulfatic deposits provide the source of sulfur. Sulfur can penetrate oxide product, and reactions are enhanced if molten sulfates are formed. Chloride, when present, disrupts the scale and facilitates easier access of the corrodant species to the underlying alloy surface. Hot corrosion represents a serious limitation for nickel-rich alloys exposed to high-sulfur partial pressures. Pitting is common, and sulfides extend deep into the alloy matrix. Products are often bulky and porous (Figure 8).

Deposits and fuel ash corrosion

Deposits and fuel ash corrosion are synonymous with many installations, including incinerators, boilers, heat exchangers, gas turbines, calciners and recuperators. Deposits introduce heat-transfer considerations for the designer and potential fouling problems for the operations engineer. When deposits become molten, corrosion processes become more severe. The immediate environment at the metal surface will be reducing, which hinders the formation of normal oxide scales.

Deposit chemistries are often complicated. Mixed compounds and eutectics often melt below 600°C. Some of the lowest melting temperatures are noted for

the alkali metal pyrosulfates, as low as 280°C; the alkali-iron trisulfates at 590 to 705°C; and the alkali metal vanadates, as low as 535°C. These temperatures are too low for normal oxidation, so protective scales may not form. Table 5 provides further melting point information.

Residual fuel oils can create deposits rich in vanadium. Some crude oils contain vanadyl vanadates. These form low-melting alkali metal vanadyl vanadates (Table 5). They effectively dissolve any protective oxide inherent to the high-temperature alloy. Normal boiler and gas turbine practice is to avoid these fuels if at all possible. Otherwise, temperatures are maintained below the range where molten products are expected. Additives such as magnesium oxide are also used to combat deposit formation by forming higher melting products. Highly alloyed materials with 50% chromium are used to resist the vanadic corrosion problem (IN-657). Chromium, silicon and chromium/aluminium coatings provide additional protection when used.

Carbonaceous environments

Carbonaceous atmospheres do not promote scale formation.[7] Instead, there is a tendency for the carbon to diffuse into the base metal (Figure 9). With time, carburisation will reduce ductility and creep resistance. Corrosion resistance may also be reduced because of chromium depletion due to local chromium carbide formation. Significant differences in thermal expansion coefficient can occur between an unaffected core of material and a heavily carburised zone nearer to the tube surface. This, together with the large volume increase that occurs during carburisation, contributes to a propensity for cracking from internal stresses. Total rupture can occur (Figure 2).

Carburisation is important for steam-methane reforming (ammonia synthesis) and ethylene pyrolysis plant (Table 3). Tube temperatures may be between 900 and 1150°C. Nickel and silicon are useful for resisting carburisation. The materials of interest include the cast high-chromium, high-nickel steels (types HH, HK, HP, with up to 35% nickel, 25% chromium and 1.5% silicon). Nickel-based alloys, cast or wrought, include alloys 800, 800H, and Incoloy DS (iron with 32% nickel, 20% chromium). Recent alloys reported to serve well include alloys RA 85H and Haynes HR-160 (with high silicon content) (Table 1). Cast tubes perform better when their interior surfaces are bored out to a smoother finish. Oxide scales are also beneficial, if present. Aluminised coatings are used for their carburising resistance.

Gas compositions rich in carbon monoxide compared with carbon dioxide introduce rapid localised damage called "metal dusting". Whole grains of metal are dislodged and the surface can be sugary to touch. Damage occurs at about 500 to 800°C. These low temperatures confine carbon nearer to the surface so no deep penetration occurs. The local reducing conditions preclude any oxide presence. Austenitic alloys, like types 300 and 400 stainless steels and alloy 800, can be so affected. Steam, ammonia, or sulfur additions to the gas stream reduce the susceptibility of attack.

Part-reducing and part-oxidising environments can result in another form of damage referred to as "green rot". The term describes the green fracture surfaces

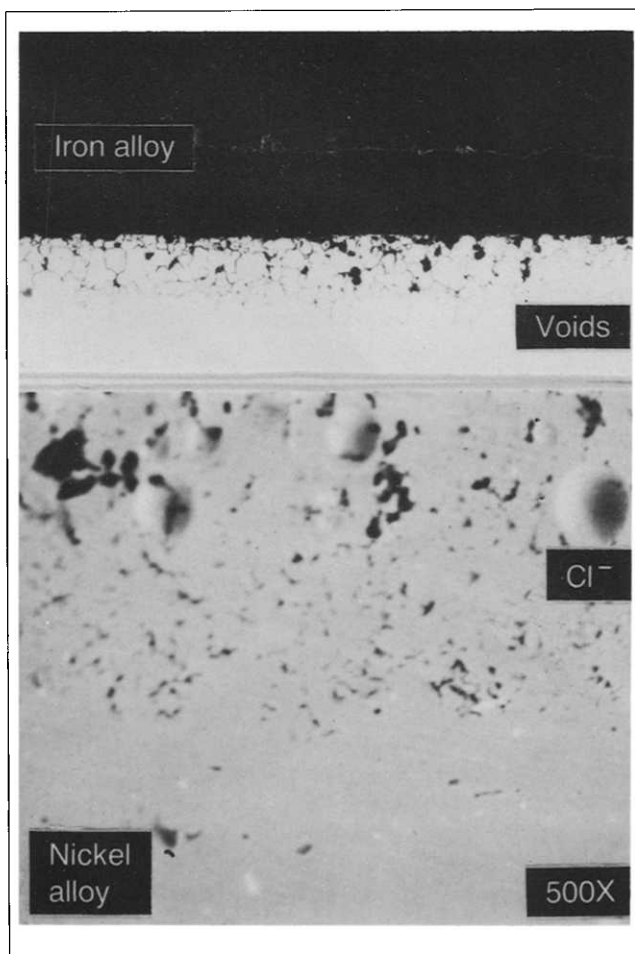Fig 9 Carburised cast reformer tube after about 10,000 hours service

Fig 10 Representative features in cross sections of iron- and nickel-based alloys exposed to chlorine vapours at a high temperature (750°C). Note the internal penetration with voids. Chloride is found within the alloy-affected zone (Photo: A Ansari/A Prescott)

where chromium oxide forms following a precarburising exposure. Damage occurs between 900 and 980°C. It has been noted following "start-up" periods where incomplete combustion may be expected.

Halogens

Halogen reactions with metals are less studied and

Table 6 Summary of Halid vapour pressure data[8] (temperatures where vapour pressure is 10^{-4} atm)

Compound	Chlorides	Fluorides	Bromides
FeX_2	536	906	509
FeX_3	167	673	156
NiX_2	607	939	580
CoX_2	587	962	–
CrX_2	741	928	716
CrX_3	611	855	615
AlX_3	76	825	53
WX_5	72	–	–
TaX_5	80	37	145
NbX_5	81	43	151
MoX_5	58	24	–

material performance criteria are still being developed. The general mechanism of corrosion is the same as for oxidation and sulfidation. Scales do not generally form because the products are too volatile and vaporise.

Halogen species are very mobile and are more permeable in a metal than oxygen. The solubility (N_x)/diffusivity (D_x) product, $(N_x D_x)$, for fluorine in nickel is about five times that for oxygen, and twice that for chlorine, at 750°C. This accounts for the predominant internal oxidation damage by fluorine as noted in Figure 2.

Chlorides tend to disrupt scales as a result of their high vapour pressures. A rapid outward migration of chloride species leaves vacancies within the alloy. The vacancies coalesce to form voids that can contribute to reduced scale adhesion. Grain-boundary penetration is a common feature reported for iron- and nickel-based alloys. Oxide scales that form when air (oxygen) and halogen coexist are porous and friable and are thus considerably less protective than those formed in oxidation. Figure 10 shows some representative features.

A common guideline for optimising materials for halogen service is to define the temperature at which the vapour pressure reaches 10^{-4}atm.[8] Representative data (Table 6) show that many common elements have high vapour pressures below 600°C. Fluorides are more stable.

Nickel-based alloys are the first choice for combatting halogen corrosion. Aluminium-containing alloys, notably alloy 214 (16% chromium, 4.5% aluminium, trace yttrium, balance nickel), have been useful. Nickel, low chromium, high molybdenum alloys (N, H-242) are good for HF-F. As with all complex areas, each case needs careful consideration. Some halogen atmospheres result in hygroscopic products that can sustain further corrosion under ambient conditions.

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