

**Oxidation of Alloys in
Steam Environments
- A Review**

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NPL Materials Centre

ABSTRACT

Traditionally materials designed for use at high temperature have been developed primarily for their mechanical properties but there is now a growing realisation that oxidation may limit lifetime. The purpose of this report is to review existing information regarding oxidation of alloys, which are intended for use at high temperatures, under atmospheres containing steam or high water vapour content and to identify areas where more understanding is required.

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Approved on behalf of the Managing Director, NPL
by Dr Colin Lea, Head, NPL Materials Centre

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1 Introduction

During service in high temperature plant, tubing, piping and headers in boilers are exposed to steam at high pressure flowing at high rates and often in the presence of heat flux. Similarly components in steam turbines are exposed to high-pressure steam atmospheres.

Service lifetimes of these components may be limited by creep, fatigue or oxidation. Traditionally materials designed for use at high temperature have been developed primarily for their mechanical properties but there is now a growing realisation that oxidation may limit lifetime, either directly through metal wastage or indirectly through raising local temperatures (and consequently reducing creep-controlled lifetimes) due to the lower thermal conductivity of the oxide scale.

The purpose of this report is to review existing information regarding oxidation of alloys, which are intended for use at high temperatures, under atmospheres containing steam or high water vapour content and to identify areas where greater understanding is required. One of the difficulties encountered in comparing test results within the literature is ensuring that the conditions of the exposures are similar. In many cases the conditions of the exposure and/or the water chemistry were not stated, this information has been included in this review where available.

2 The Influence of Chromium Content

The most significant improvements in oxidation resistance are achieved by changing the inherent nature of the protective oxide scale. One of the most dramatic demonstrations of this mechanism is the influence of chromium additions to iron-base alloys. During oxidation, carbon steels form a scale consisting of one or more layers of wustite, haematite and magnetite depending upon the specific oxidation conditions. The addition of chromium to the alloys firstly changes the scale such that the inner layer (magnetite in plain carbon steels) is an iron-chromium spinel in low alloy ferritic (up to 3%Cr) or martensitic (9-12%Cr) steels. Further increases in chromium will eventually lead to the formation of chromia, e.g. in austenitic stainless steels.

The effect of increasing the chromium content in ferritic steels has been demonstrated in both laboratory and service exposures. Solberg *et al*¹ demonstrated a systematic decrease in metal loss with increasing chromium content in short-term laboratory tests at 593 °C. Their data are presented in Figure 1.

Similarly Eberle *et al*² demonstrated (see Table I) a similar trend in material that had been withdrawn from service after 36000 hours at 554 °C / 160 atm.

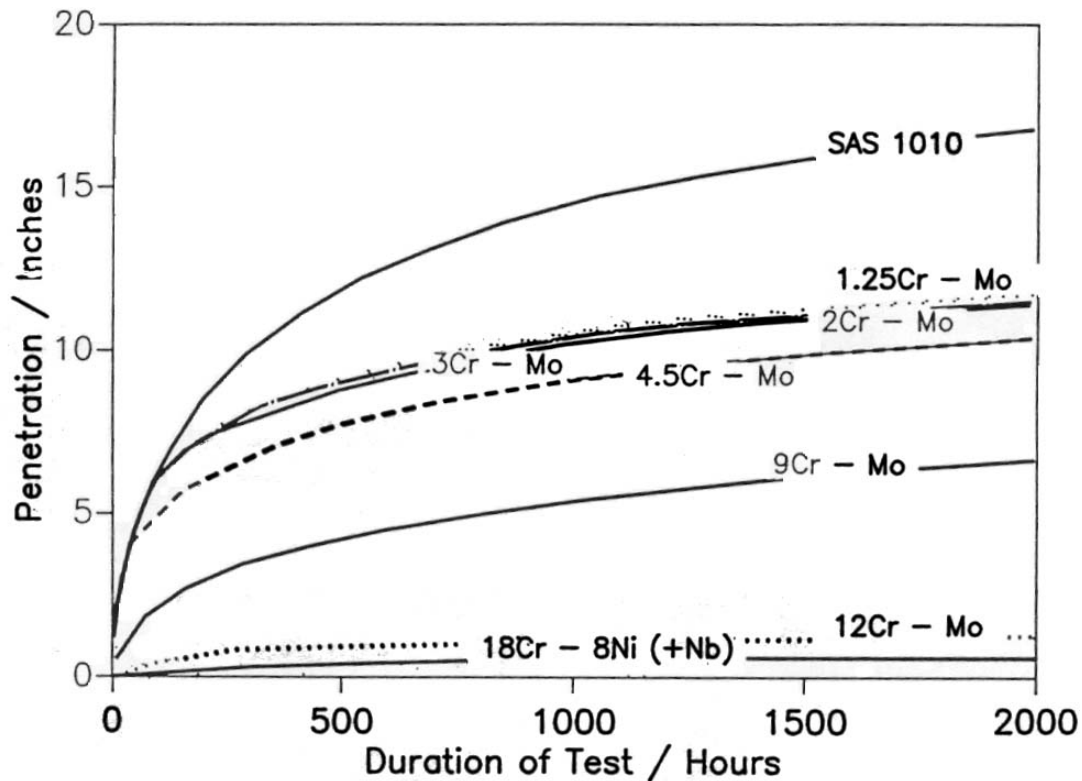


Figure 1 Corrosion of steel bars in contact with steam at 593 °C for 200, 500, 1000 and 2000 h (after Solberg *et al*¹)

Table I Metallographically measured scale thickness on exposure to steam at 554 °C/160 atm for 36000 h (after Eberle *et al*²)

Material	Inner scale, μm^*	Outer scale, μm^*	Total thickness, μm^*	Total thickness range, $\mu\text{m}^\#$
SA-210 C-steel	90	70	160	125 – 160
$\frac{1}{2}$ Mo	80	70	150	125 – 150
$\frac{1}{2}$ Cr – $\frac{1}{2}$ Mo	70	55	125	125 – 165
$1\frac{1}{4}$ Cr – $\frac{1}{2}$ Mo	75	60	135	135 – 165
$2\frac{1}{4}$ Cr – $\frac{1}{2}$ Mo	75	60	135	125 – 145
5 Cr – $\frac{1}{2}$ Mo	70	50	120	110 – 150
7 Cr – $\frac{1}{2}$ Mo	65	55	120	120 – 125
9 Cr – 1Mo	65	55	120	120 – 145

* Measured at one location

Range of measurements

Heiermann *et al*³ have also shown that there is a trend for the higher Cr-containing steels to produce thinner scales: 160 and 260 μm scales at 560 °C for 12 and 9% Cr and 290 and 510 μm scales at 600 °C for 12 and 9% Cr ferritic steels respectively after 200000 hours exposure. Thus the more Cr an alloy contains the better it can protect itself from oxidation, and therefore alloys with high Cr are usually used in corrosive environments. The improvement in steam oxidation resistance of the 9-12Cr materials over the low alloy ferritic steels is demonstrated in Figure 2⁴. At 560 °C the rate of scale growth on 9%Cr steels is half that on 2%Cr material. Increasing the chromium content to 12% produces another factor of two improvement.

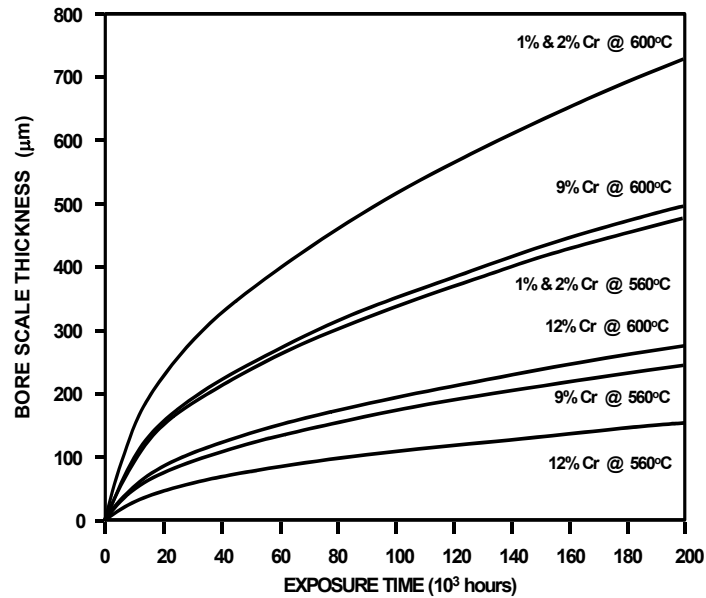


Figure 2 Bore oxide scale thickness as a function of operating time and temperature for ferritic (1-2%Cr) and martensitic (9-12%Cr) steels (after Ref. 4)

This improved protection can also be seen in Figure 3, which shows the oxidation of T22, T23, TP347, T91 and T92 in flowing pure water vapour at 650°C⁵. In this instance the samples were hung on a kanthalmade support fixed on a corundum basket, which was then placed into the mullite tubes inside a tubular furnace. The steam was produced by ebullition of deionised water. The corrosion rates of the steels were determined by mass change measurements prior to and after exposure and descaling by etching in sodium hydroxide melted at 450 °C⁴.

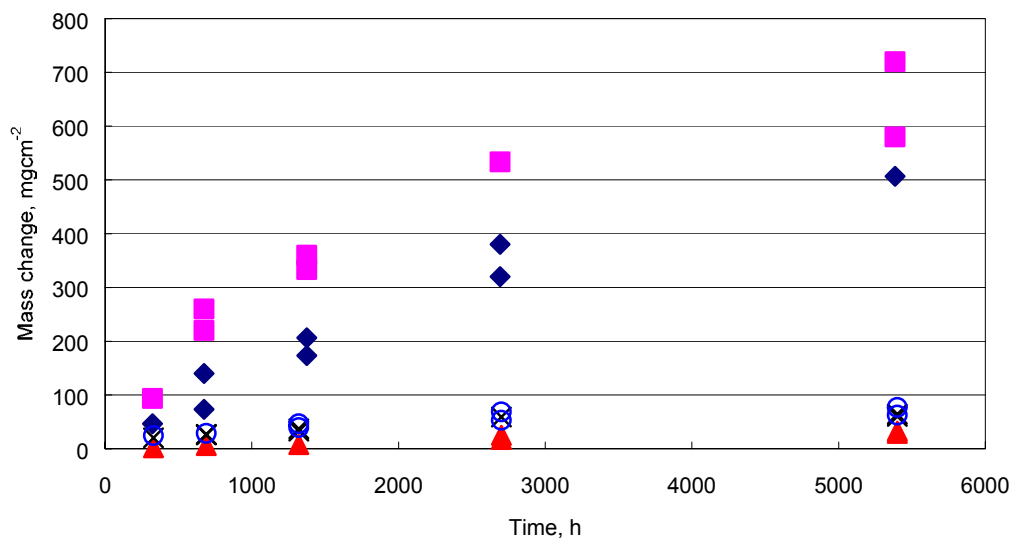


Figure 3 Oxidation in flowing pure water vapour at 650 °C (after Ref 5)

Manning and Metcalfe⁶ have also demonstrated this improvement when they compared the parabolic rate constants of 2¼Cr1Mo with 9Cr1Mo and 12Cr ferritic steels over the

temperature range 500 – 700 °C. A significant reduction in the parabolic rate constant with increasing chromium content from 2¼ to 9% is seen at the higher end of the temperature range but the difference between the two alloy classes is less marked at lower temperatures.

However, there also exists a body of contradictory evidence of oxidation behaviour of the 2¼Cr-1 Mo steel and the 9Cr. The small improvement in oxidation properties brought about by increasing the Cr content from 2¼ to values characteristic of the 9%Cr alloys was highlighted by Griess and Maxwell ⁷ who claimed that from purely a steam oxidation standpoint there were no significant differences in the corrosion rates. This observation came from work they conducted, where selected alloys were exposed to plant steam, from the Bartow Power Plant of the Florida Power Corporation. Samples of a 2¼Cr-1 Mo steel were prepared from mill-annealed plate. A selection of these were annealed (732 °C for 2 h and then furnace cooled) whilst the others were pickled. No significant differences arose from the different surface treatments as shown in Figure 4, where the similar oxidation behaviour of the 9Cr steel can also be seen. The oxidation kinetics initially follow a parabolic rate law, until around 5000 hours, at which point the oxidation rate becomes more linear.

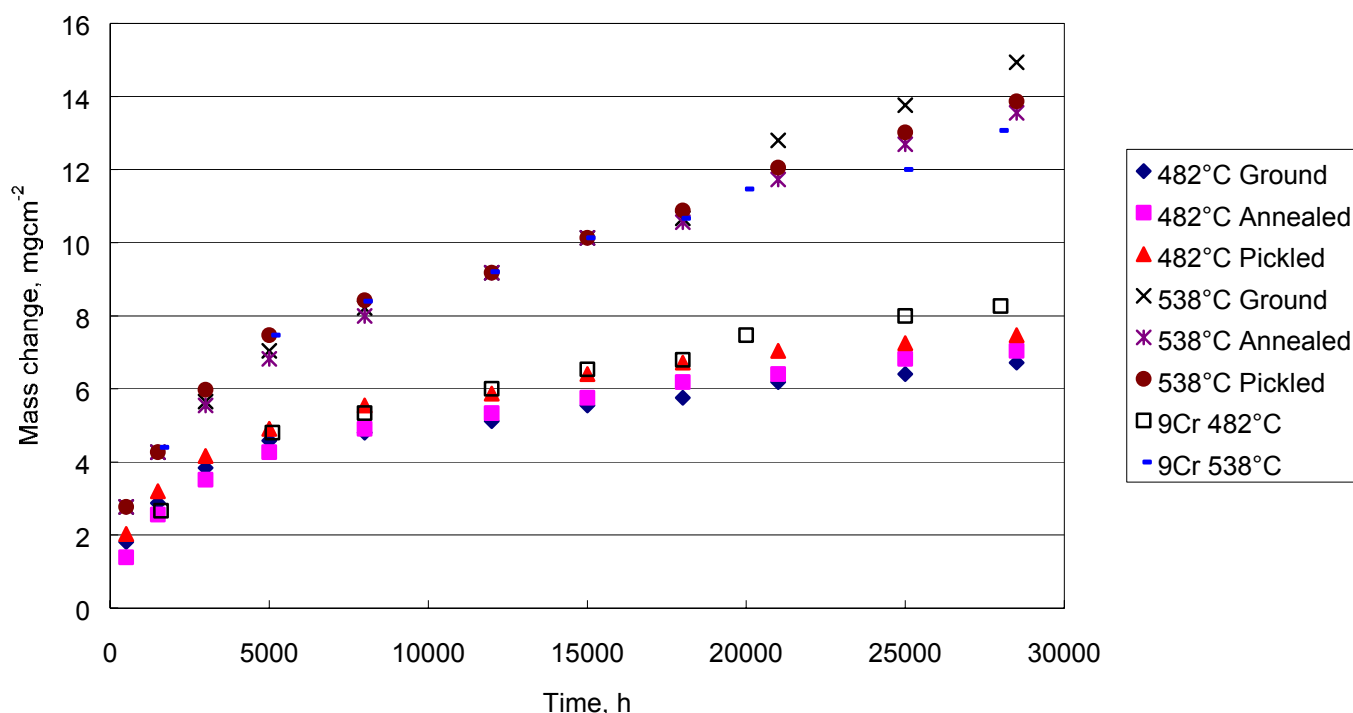


Figure 4 2¼Cr1Mo and 9Cr steels exposed to superheated plant steam (after Ref. 7)

It appears that the level of benefit arising from increased chromium content is not constant but is dependant on the moisture content of the oxidising atmosphere. To illustrate this point when comparing the oxidation in steam of the low Cr containing alloys T22 and T23 to the higher Cr containing ferritic steels it has been reported by Gambier ⁸ that the corrosion rates of the 9% Cr steels were only about 3 times lower than those of the 2¼% Cr steels. These results clearly demonstrate the deleterious effect of water vapour since the corrosion rate in air is usually 60 – 70 times lower for 9Cr steels than for 2¼ Cr steels. This reduction of the favourable effect of Cr in steam compared to in air has been attributed to changes in the morphology of the oxide scales developed in steam environments. Lepingle ⁵ showed that

within such oxide scales there existed a large number of macroscopic defects, such as pores, cracks etc.

Whilst it is evident that water vapour does increase the oxidation kinetics it is also true that the presence of high levels of Cr in the alloy does still impart some enhanced protection.

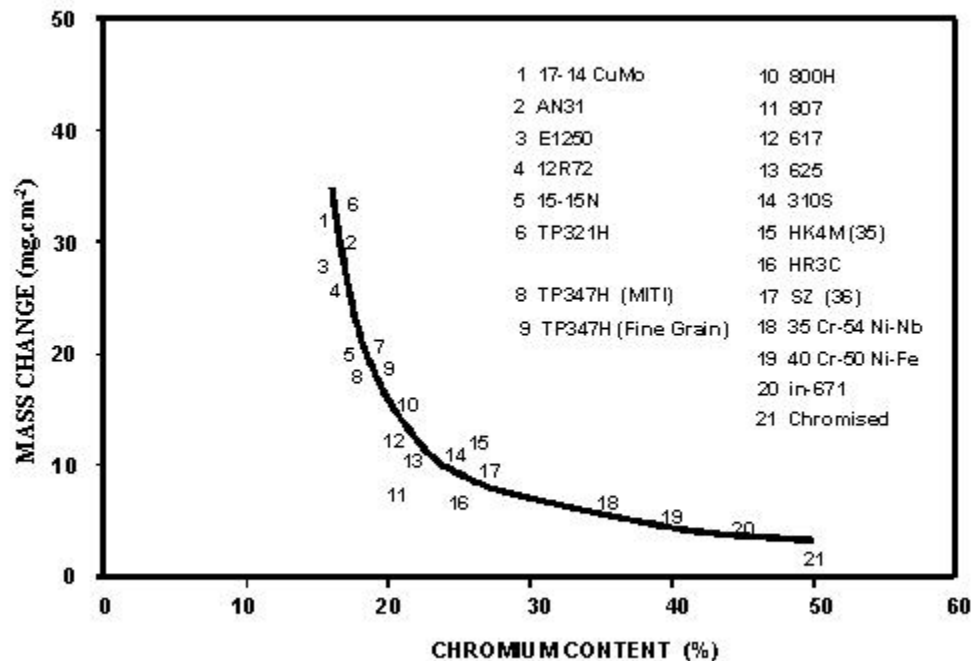


Figure 5 Metal loss rate as a function of chromium content for selected materials under simulated fireside corrosion conditions (after Ref. 5)

In the case of alloys with Cr content over 12% benefits in steam oxidation resistance have again been observed from increases in the Cr content. Tests have shown that increasing the Cr content from 12 to 18% increased the duration of the protective stages of some alloys from 1 hour to more than 25 hours. In studies by Tavast⁹ and Otsuka and Fujikawa¹⁰ it was concluded that if the Cr content was over 25% (Otsuka quotes 22%), then a continuous chromia layer quickly forms at the metal-metal oxide interface, slowing down the diffusion of iron to form magnetite at the gas-metal interface. This is a general rule and there will be exceptions. For example, in a comparative study the austenitic steel TP347 was found to have mediocre corrosion resistance, despite its high level of Cr content⁵. The relatively poor behaviour was attributed to corrosion product scaling phenomena and the non-uniform healing of the chromia layer during the test (this has also been observed by Armanet¹¹, Montgomery¹² and Otsuka¹⁰). This may suggest that there is a limit to the maximum amount of Cr that is beneficial in terms of scale adherence. Figure 5 shows the metal loss rate for alloys with differing amounts of Cr. The data show how the amount of metal loss decreases with increasing Cr content and approaches a plateau level, thus illustrating an upper limit to the benefits of Cr additions.

3 Low Alloy Ferritic Steels

Low alloy ferritic steels are most widely used in pressurised applications in boilers fired by fossil fuels and also in Heat Recovery Steam Generators (HRSG's). Specifically these are tubing alloys that are used particularly in the cooler sections of superheaters and reheaters and also for the waterwalls in the temperature range where mild steel becomes too susceptible to creep. These alloys are also used in thick-section components such as headers and steam pipes.

Commonly the key requirements that this class of material must exhibit are

- Good tensile strength (120 MPa) at temperatures up to 450 °C
- Creep strength at temperatures up to 550 °C (T22, T23)
- Excellent weldability with no requirement for post-weld heat treatment
- Resistance to steam oxidation

For the purpose of this review the most pertinent of the above requirements is the resistance to steam oxidation. These materials do have limited resistance to steam oxidation, and improving this resistance would result in enhanced heat transfer and increased operating temperature, thereby contributing to increased plant efficiency with little increase in cost. Table II shows the composition of some common low alloy 1-3% Cr steels, together with commonly used alternative nomenclature of these alloys.

Table II Composition of Low Alloy 1-3% Cr Steels

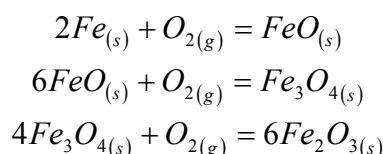
Alloy	Alternative Nomenclature		Composition, wt%												
			C	Mn	P	S	Si	Cr	Mo	V	N	Nb	W	B ppm	Al
Grade 11	P11/T11/13CrMo 4 4	Min	0.05	0.3			0.5	1.0	0.44						
		Max	0.15	0.6	0.025	0.025	1.0	1.5	0.65						
Grade 22	P22/T22/10CrMo 9 10	Min	0.05	0.3				1.9	0.05						
		Max	0.15	0.6	0.025	0.025	0.5	2.6	1.13						
Grade 23	P23/T23/HCM2S	Min	0.04	0.1				1.9	0.05	0.2		0.02	1.45	5	
		Max	0.1	0.6	0.03	0.01	0.5	2.6	0.3	0.3	0.03	0.08	1.75	6	0.03
Grade 24	T24/7CrMoVTiB 10-10	Min	0.05	0.3			0.15	2.2	0.9	0.2				15	
		Max	0.10	0.7	0.02	0.01	0.45	2.6	1.10	0.3	0.012			70	0.02
1CrMoV			0.25	0.8	0.01	0.02	0.2	1.0	1.0	0.3	0.004				0.01

The scale formed during steam oxidation of low alloy steels has three distinct regions when cross-sectioned. These comprise a thick compact outer layer, a subscale region consisting of extensive internal oxide precipitate formation mostly along the grain boundaries, and a thin layer between the outer layer and the subscale. It is claimed that a critical balance of the selectively oxidised metal, the oxidant species and the growth rate of the external scale govern the extent of the internal oxide precipitation and subscale formation¹³.

There is a distinct difference in the structure and morphology of the oxide scales formed under 'dry' air oxidation and steam oxidation. In terms of the morphology of the oxide scales a recent study conducted by Raman¹⁴, in which specimens were oxidized at 600 °C in a

mixture of steam and nitrogen, reported that the scales developed during steam oxidation on 2¼Cr-1Mo steel consisted of faceted oxide grains, whilst the morphology of the air-oxidised specimens were reported to be featureless. The structure of the scales on the steam oxidised specimens, it was noted, were free from surface pores and the oxide grains were closely compacted to each other. This is distinctly different to the porous outer scales observed under air-oxidation.

General observations have indicated that the oxide scale, which forms on the steam side surface of carbon steel boiler tubes, is generally found to consist of a multilayered scale ¹⁵. The composition of the scales is predominantly magnetite and wustite (Fe₃O₄ and FeO respectively); however there is also evidence in XRD patterns of the presence of an iron-chromium spinel oxide (FeCr₂O₄). More specific observations have indicated that at temperatures below 560 °C a scale consisting of magnetite (Fe₃O₄) and haematite (Fe₂O₃) is found. At higher temperatures an additional inner layer of wustite (FeO) may be present. If the tubing in question is alloyed then a spinel oxide (Fe, Cr, Mo)₃O₄ will form as the oxide grows inward across the tube wall ¹⁵. These form as follows:



Current understanding has it that the wustite formation temperature is assumed to be a constant of 560 °C, independent of the alloy in question. In work conducted by Aríztegui *et al* ¹⁶ isothermal and non-isothermal tests were conducted on 2¼Cr-1Mo steel (T22) that confirm the above observations. They found that in isothermal tests in the temperature range of 550 to 700 °C over exposure periods of up to 56 days, that magnetite was the most stable oxide at the lower temperatures. Their observations are presented in Table III.

Table III Oxide products present in the oxide scales formed after isothermal oxidation treatments
(after Ref. 16)

Exposures time (days)	Temperature			
	550 °C	600 °C	625 °C	650 °C
7	M+H	M/W	M	W/M+W
14	M+H	M	M+(W)	/
28	M+H	M	M+W	M+W
56	M	M	M+W	/

M – magnetite, H – haematite, W – wustite.

In the experiments performed by Aríztegui *et al* ¹⁶ a constant flux of high purity argon was used to carry the steam through three conduits. The first fed into a “reference tube” in the furnace, in which the sample was exposed to high temperatures in the absence of steam. The remaining two identical conduits flowed through a water flask before reaching the furnace thereby producing an Argon / steam mixture.

Under isothermal conditions the oxidation kinetics not surprisingly followed a parabolic rate law, with calculated activation energy of oxidation calculated from the scale thickness of 324 kJ mol⁻¹ (308 kJ mol⁻¹ from weight gain data), this value is reported to agree well with

other documented values and it is claimed to be consistent with a reaction controlled by diffusion during which passivation of the metal takes place¹⁷⁻¹⁸. X-ray diffraction analysis showed that magnetite was formed at any temperature from 550 °C to 650 °C, but for temperatures greater than 570 °C wustite was found to be forming beneath the magnetite layer. Its formation, it was suggested, could be interpreted as a reaction between oxygen and Fe at the reaction interface in two ways:

1. Oxygen permeated through the oxide layer to react with the iron, or
2. An internal reaction between Fe_3O_4 and Fe ($\text{Fe}_3\text{O}_4 + \text{Fe} \rightarrow \text{FeO}$) due to destabilisation of the Fe_3O_4 at high temperatures.

No preference was established. After non-isothermal treatment, which consisted of a week long exposure at 550 °C followed by a period of between 8 to 24 hours at 700 °C, the scale that formed was found to be very irregular due to cracking. The analysis of the data indicated that a passivating oxide was formed in the first (non-isothermal treatment) cycle, as subsequent deviations in the temperature had no effect on the oxidation kinetics. In terms of the phases present in the oxide, these are presented in Table IV.

Table IV Oxide products present in the oxide scales formed after non-isothermal oxidation treatments (after Ref. 16)

Time spent at 550 °C + 700 °C	Slow Cooling	Rapid Cooling
7 days + 4 hours	M/M+(W)	M/M+(W)
7 days + 8 hours	/	M/M+W
7 days + 24 hours	M/M+W	M+W/W+M
7 days + 4 hours + 7 days 550 °C	M+H/M	/

M – magnetite, H – haematite, W – wustite.

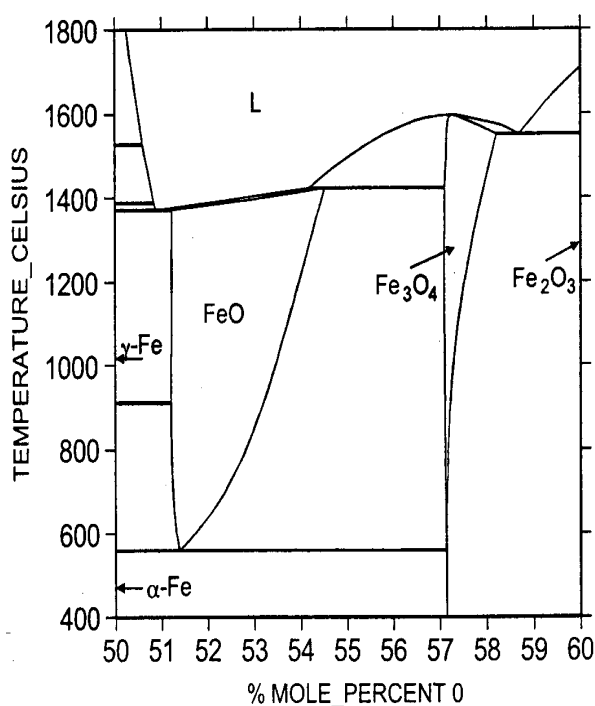


Figure 6 Iron-Oxygen phase Diagram

In the case of the non-isothermal treatments the relative amounts of these constituents, as presented in Table IV, seemed to be dependent on the cooling rate and the temperature of the treatment. It should be noted that the type of oxides formed within this work were in agreement with that which would be expected from the iron-oxygen phase diagram shown in Figure 6.

It is generally found that when exposed to flowing steam these low alloy materials follow a parabolic growth rate law at temperatures below 600 °C, i.e. consistent with the work in Ar/steam. Nava-Paz and Knoedler ¹⁹ compared the steam oxidation behaviour of Grades 22 and 23. They observed identical parabolic growth kinetics in both materials under flowing steam atmospheres at 600 °C, the rate constant was quoted as being $5.2 \times 10^{-11} \text{ g}^2 \text{ cm}^{-2} \text{ s}^{-1}$. They found that thermal cycling did not accelerate the oxidation rates; this may be explained by the observation made by Ariztegui *et al* ¹⁶ in Ar/steam where a passivating oxide formed in the first few cycles.

In contrast, when tested in stagnant steam they found that the materials followed different growth kinetics, with Grade 23 following a cubic rate law (time exponent = 0.33). However there is some doubt about the reliability of testing in stagnant steam because of the effect of concentration of impurities etc. It is also apparent from this review that the results obtained from different experimental techniques can differ greatly, this will be illustrated at a later point.

In test conducted using pure water vapour Lepingle *et al* ⁵ exposed six grades of steels at temperatures of 500, 550, 600 and 650 °C for 5376 h (32 weeks). The steels that they compared were T22, T23 and the higher Cr alloys of T91, T92, T122 and TP347. The corrosion rates were determined by mass change measurements, and an example of the results obtained is shown in Figure 7.

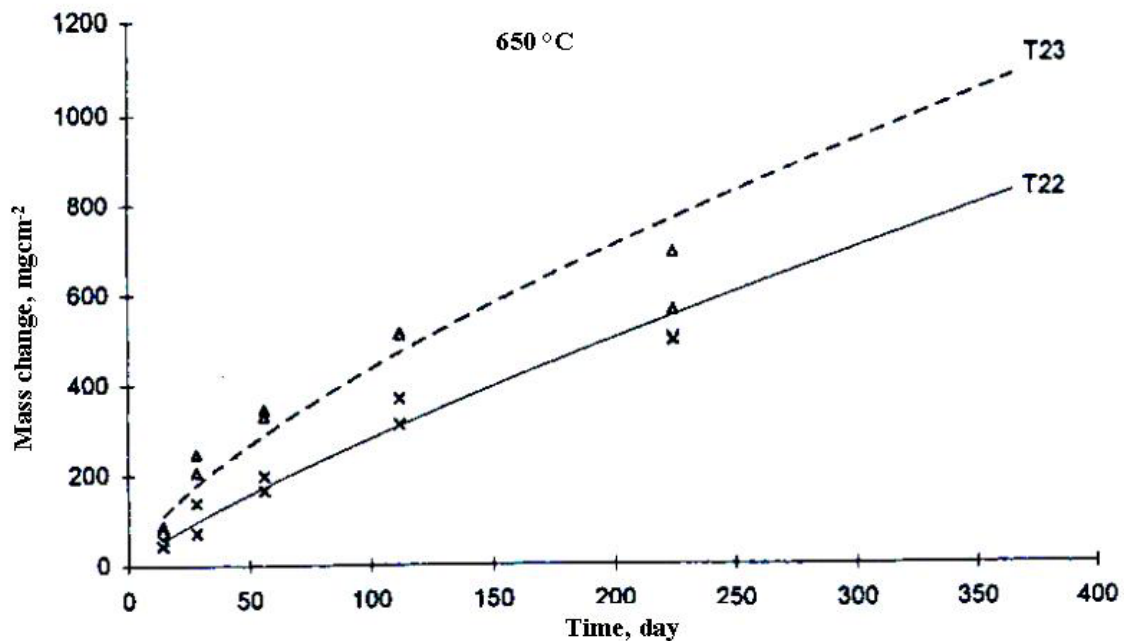


Figure 7 Mass change of T22 and T23 steels in water vapour at 650 °C (after Ref. 5)

The rate calculations performed were in agreement with the earlier work conducted by Nava-Paz and Knoedler¹⁹ with T22 and T23 having the exponent 'z' value as shown in Table V.

Table V Calculated values of the 'z' exponent of the relationship $\Delta m = kt^z$ (after Ref. 5)

Steel	'z' exponent at...			
	500 °C	550 °C	600 °C	650 °C
T22	0.46	0.49	0.62	0.83
T23	0.41	0.41	0.71	0.71

This suggests that at temperatures below 600 °C, T22 and T23 obey a parabolic law, which indicates that at these temperatures the materials are self-protecting. However at high temperatures the scale becomes non-protective and the kinetics approach linear behaviour. Although interesting this material class is rarely used at such elevated temperatures.

Although many of the reported relationships claim to be following parabolic rate laws, others rate laws have been cited i.e. logarithmic, combined functions etc. In a report by Bueno and Marino²⁰ data relating to steam oxidation from three different sources were compared with their own 'dry' oxidation data. Figure 8 shows three graphs comparing the four sets of data. In each plot the 'dry' oxidation data of Bueno and Marino²⁰ has been compared to different oxidation rate laws suggested by other authors²¹⁻²², namely parabolic (plot a)²¹, logarithmic (plot b)²² and as a combined function (plot c)²². It is apparent that there is much disagreement between them; and that the presence of steam greatly affects the observed reaction kinetics. Interestingly, the data indicate that the oxidation rate changes around 700 °C, such that at 600 °C $k_p \text{ dry} > k_p \text{ steam}$, whilst at 700 °C $k_p \text{ dry} \cong k_p \text{ steam}$ and at 800 °C $k_p \text{ dry} < k_p \text{ steam}$.

Data in the literature are generated using three main experimental methods to produce high temperature steam environments, static steam, pure flowing steam and a mixture of steam and a carrier gas. The oxide scales formed and the oxidation rate are dependant on which method is used and the temperature of the test. To illustrate this consider Figure 9, which shows the oxidation rate at 600°C for T22 and T23 in air²⁰, pure water vapour⁵ and a mixture of steam and argon¹⁶.

It is clear from Figure 9 that:

- Steam has a deleterious effect on the oxidation
- T22 appears to oxidise faster in pure steam than in a mixture of steam and argon
- The kinetics are parabolic indicating that the passivating scale is not spalling in all cases

The difficulty comes in determining which exposure method best replicates the in-service conditions, in terms of both the oxidation rate and the morphology of the resultant oxide scale. From the literature examined there is no consensus on these points and also little mention of the potential effects of steam chemistry.

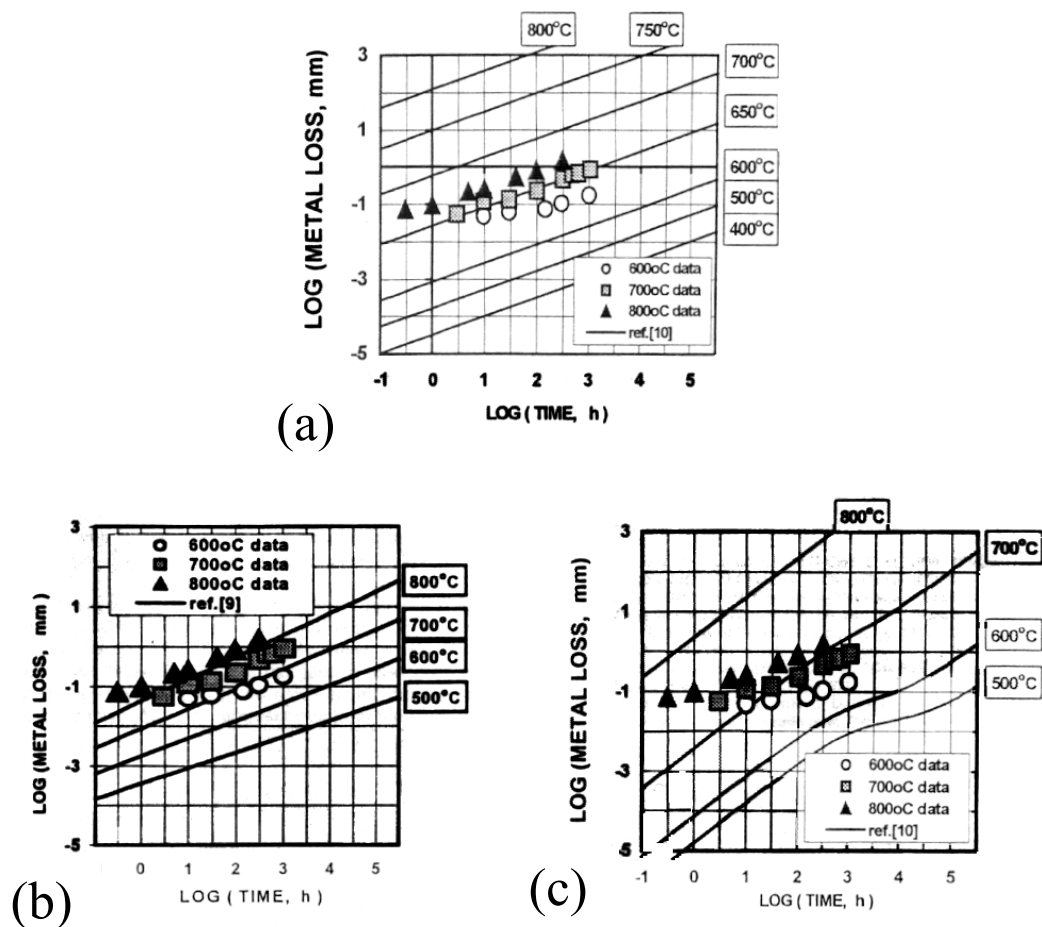


Figure 8 Comparison of data obtained from four separate works, illustrating how different rate laws can be used. The symbols show 'dry' oxidation data compared rate laws under steam oxidation conditions. Plot (a) shows a parabolic rate, (b) logarithmic and (c) is a combined function. All data relates to 2 1/4Cr-1Mo steel (After Ref. 20)

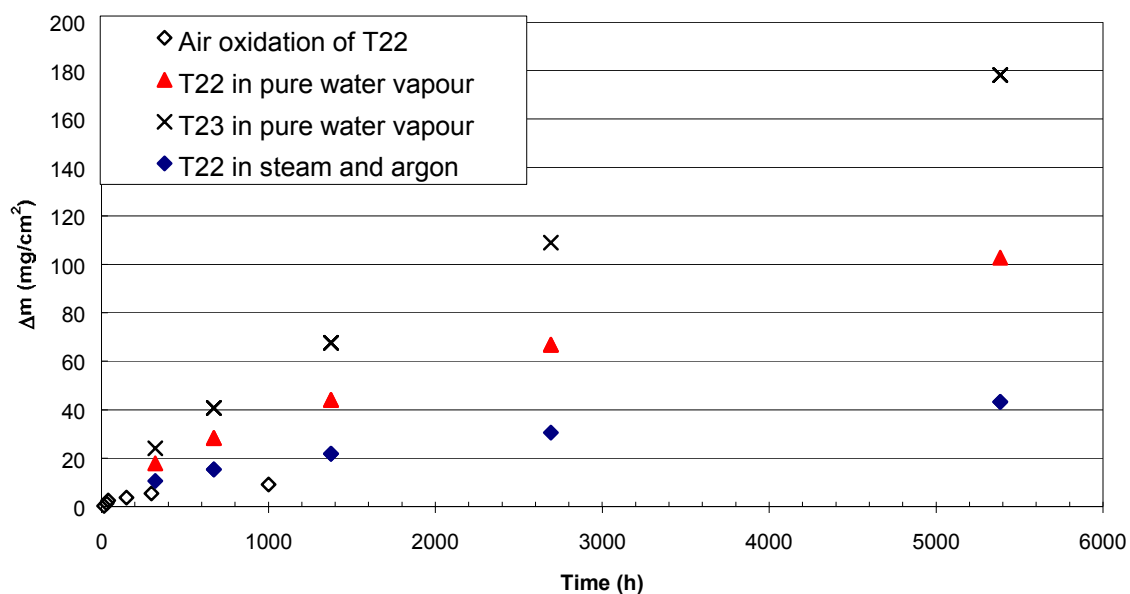


Figure 9 Comparison of oxidation rates at 600°C using different exposures

From the available literature several main points can be drawn. The growth kinetics are affected by several factors; (1) the flow rate of the steam atmosphere, (2) temperature, they range from sub parabolic at low temperature (500 °C) to approaching linear at 650 °C, (3) composition of the test environment, the presence of water vapour in the test atmosphere may increase or decrease corrosion rate, depending on test temperature.

4 9-12% Cr Martensitic Steels

The 9-12% Cr steels are used in both boilers and in steam turbines where the alloys used are exposed to high pressure steam environments at temperatures up to 620 °C and pressures in excess of 300 bar.

In boilers that use fossil fuel these steels are used for tubing in superheaters and reheaters, operating with metal temperatures up to about 620 °C.

In boilers for nuclear operation the steels are again used for tubing in superheaters. However, in this case the temperatures are lower, typically 520 °C.

In steam turbines, alloys of this type are used for rotors and blading but also in cast form for steam chests and valve bodies.

The morphology of the scales formed by this class of alloy is often found to contain macroscopic defects such as pores, cracks etc ⁵. Further examination of the oxide scales conducted by Lepingle ⁵ using XRD, SEM and EDX analysis is reported to have shown that the corrosion products on T91, T92 and T122 steels have an Fe-rich outer layer with an inner layer that consists of Cr, Mo, Fe oxides. Furthermore in T91 and T92 steels this inner layer is in itself split into two layers, the one close to the metal was found to be oxygen-depleted ⁵.

As with the low alloy ferritic steels the oxidation kinetics of martensitic steels have been shown to follow parabolic rate constants. Montgomery and Karlsson ¹² compared the parabolic rate constants of 5 commercial martensitic steels viz 9Cr1Mo, T91, X20, T92 and HCM12 over a range of temperatures and pressures. Typical compositions of the 5 alloys are given in Table VI. The data are shown in detail in Figure 10 and summarised in Figure 11. The apparent spread in the results within particular alloy subsets was attributed to factors that may not have been reported, such as surface preparation etc. The exact conditions of the steam exposure were not given in the paper.

Data were also presented from tests that were carried out at different steam pressures. No significant influence of steam pressure was observed although the authors commented that in some cases a slight increase in parabolic rate constant is observed with increased steam pressure.

Table VI Composition (wt%) of 5 commercial martensitic steels

	C	Mn	Si	Cr	Mo	V	N	W	B	Ni
9Cr1Mo	0.12	0.45	0.6	9	1.0					
T91	0.1	0.45	0.4	9	1.0	0.2	0.049			0.8
T92	0.07	0.45	0.06	9	0.5	0.2	0.06	1.8	0.004	
HCM12	0.1	0.55	0.3	12	1.0	0.25	0.03	1.0		
X20	0.20	1.0	0.5	12	1.0	0.3				0.6

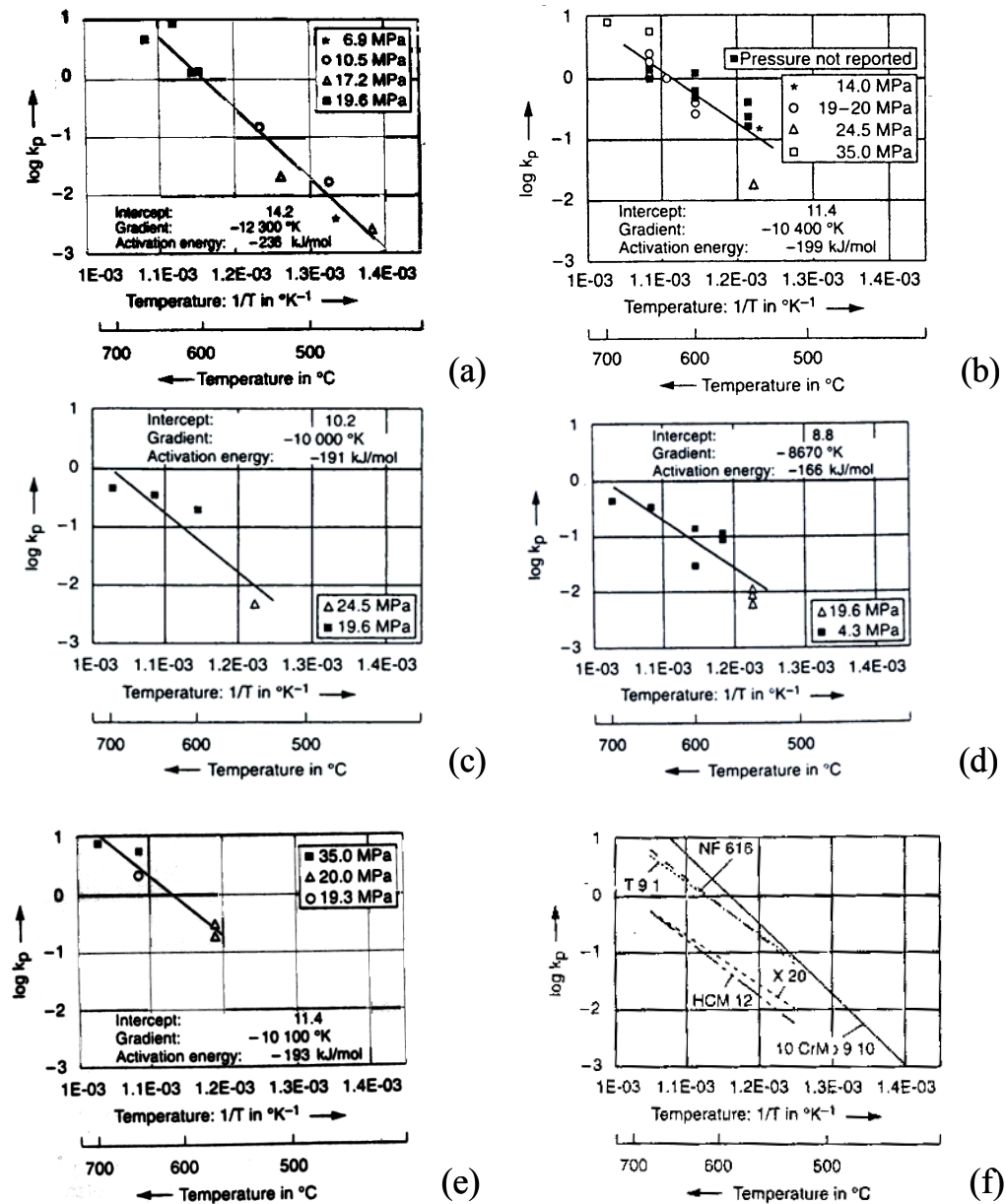


Figure 10 Arrhenius plots of steam oxidation constants for (a) 10CrMo910 (T22), (b) X10CrMoVNb91 (T91), (c) X20CrMo121, (d) HCM12, (e) NF616 and (f) comparison of all the previous materials (after Ref. 12)

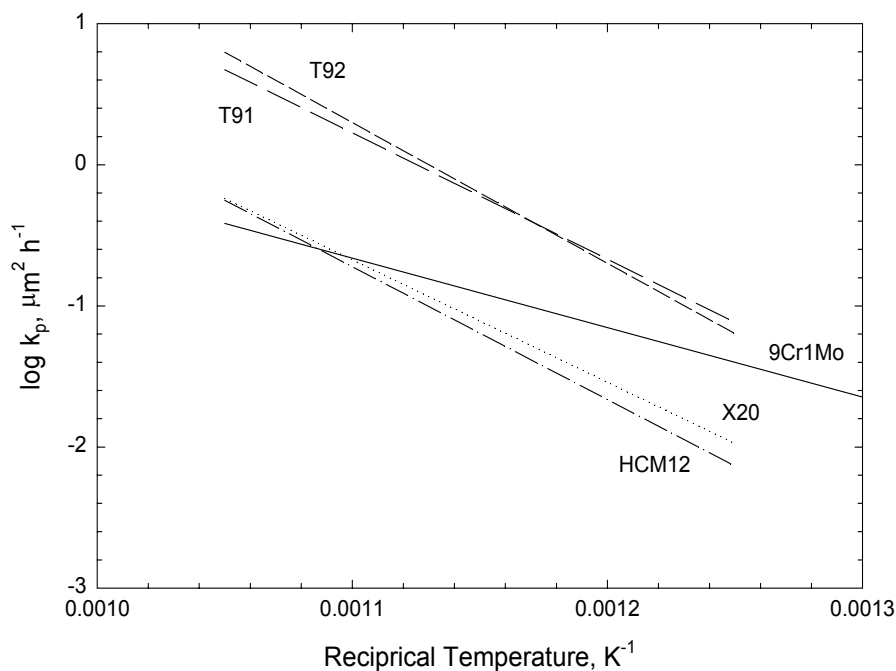


Figure 11 Parabolic rate constants for several steel alloys

Comparison of the relative oxidation rate of the steels containing 9%Cr shows that 9Cr1Mo is substantially better than T91 and T92, with the improvement increasing with increasing temperature. This observation implies that one or more of the additional alloying elements in T91 and T92 i.e. V, W or Ni, is detrimental to steam oxidation resistance.

Abe *et al*²³ studied the influence of minor alloying additions on the steam oxidation behaviour of a 9%Cr steel at 600 and 650 °C. Si additions improve the steam oxidation resistance but have the deleterious effect of encouraging carbide agglomeration. The addition of trace amounts of Ti or Y(0.05%) further improve the steam oxidation resistance of alloys containing 0.5% Si (Figure 12)²³.

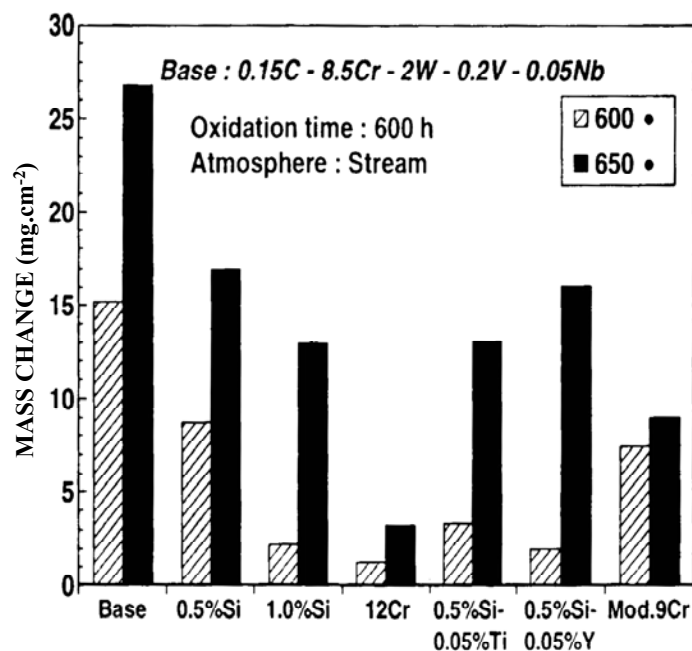


Figure 12 Mass change of the steels during oxidation at 600 and 650 °C (after Ref. 23)

The beneficial effect of additions of silicon to the alloy composition has also been reported by Hurst and Cowen²⁴. To further investigate this Griess and Maxwell⁷ exposed a selection of alloys containing a range of silicon concentrations to superheated steam at temperatures of 482 °C and 538 °C. The results are presented in Table VII. Although the exposure time was short, it is interesting to note that the mass gains were generally lower for higher silicon contents, an example of this is shown in Figure 13 for 9Cr-1 Mo steel.

Table VII Average mass gains of duplicate Cr-Mo steel specimens in superheated steam (After Ref. 7)

Designation	Silicon content (wt%)	Temperature (°C)	Average weight gain (g/m ²)		
			997 h	2556 h	5729 h
5 Cr-1 Mo	0.11	482	19.1	23.3	36.4
		538	35.2	47.8	75.1
	0.14	482	18.1	22.6	35.4
		538	34.7	46.4	73.1
7 Cr-1 Mo	0.14	482	18.9	23.0	35.4
		538	34.2	45.2	70.0
	0.17	482	17.7	21.5	32.9
		538	33.3	44.0	70.1
9 Cr-1 Mo	0.01	482	19.0	24.4	43.0
		538	45.6	68.1	121.1
	0.02	482	18.6	23.5	39.3
		538	40.4	53.2	92.1
	0.04	482	17.9	23.1	39.8
		538	41.8	61.8	103.3
	0.36	482	15.5	18.8	29.3
		538	25.7	34.4	58.4

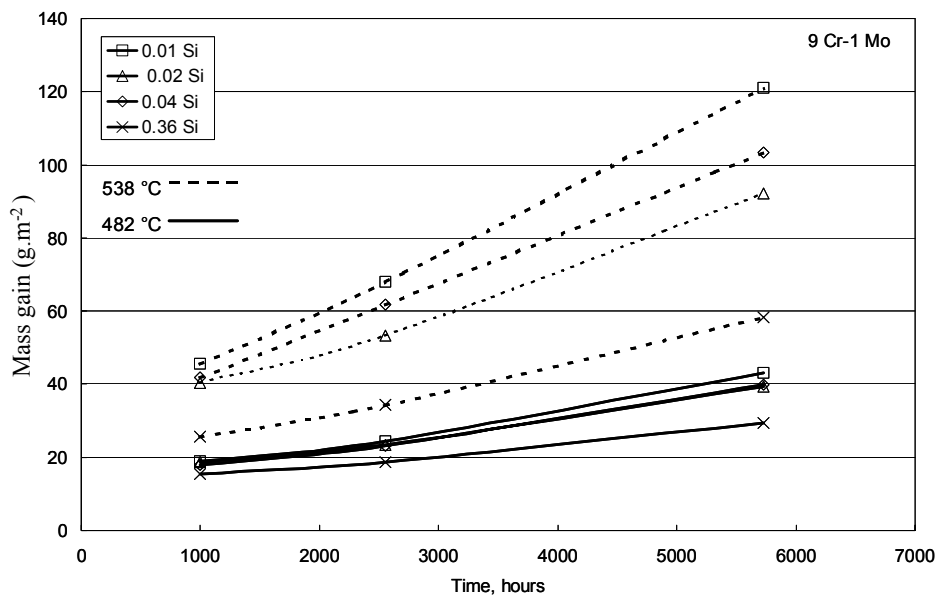


Figure 13 Affect of increasing the Si content of 9 Cr-1 Mo Steel, similar affects were exhibited by lower Cr content alloys as shown in Table VI (After Ref. 7)

Igarashi *et al*²⁵ have shown that Pd additions to 9Cr 3.3W steels improve creep resistance at over 650 °C and steam oxidation rates at up to 750 °C decreased by factor of 10.

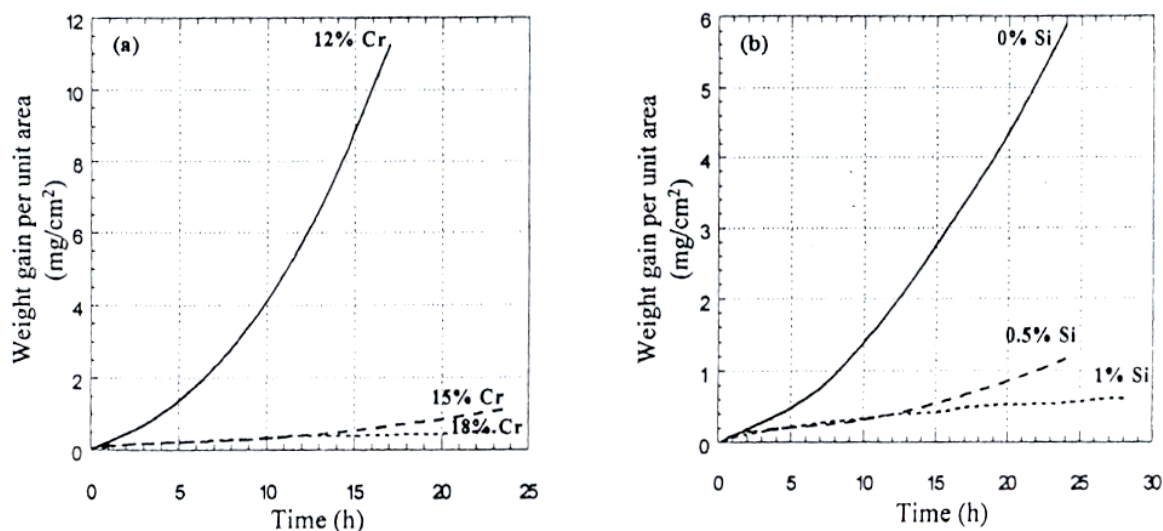


Figure 14 Oxidation curves of stainless steels with various (a) chromium and (b) silicon (for 15% Cr) contents, oxidised at 900 °C in Ar+15% H_2O (after Ref. 26)

Henry *et al*²⁶ exposed a reference steel sample to dry air, and established that under these conditions the oxidation followed a pure parabolic rate law for durations of over 400 hours ($k_p = 8.76 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$). In the presence of water vapour the same material showed breakaway corrosion after only 8 hours. Before the breakaway occurred the kinetics followed a parabolic law ($k_p = 2.42 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$) and then accelerated to a linear rate after breakaway. A comparison was then conducted to illustrate the effect of increasing the Cr content from 12 to 18% and increasing Si from 0 to 1%. In conjunction with this, a study on the effect of the water vapour partial pressure was conducted, varying the pressure from 150 mbar to 10 mbar. The results are presented in Table VIII and in Figure 14.

Table VIII Time to breakaway at 900 °C as a function of the composition of the steel and the water partial pressure (after Ref. 26)

	12% Cr		15% Cr		18% Cr	
	10 mbar	150 mbar	10 mbar	150 mbar	10 mbar	150 mbar
0% Si	Not studied		t = 5-8h	t = 2-3h	Not studied	
0.5% Si	t = 1h	t = 1h	t = 15h	t = 9h	t > 25h	t > 25h
1% Si	Not studied		t > 50h	t > 50h	Not studied	

The results showed that increasing the Si content from 0 to 1% in a Fe-15Cr alloy, increased time to breakaway from 2 hours to more than 50 hours. Decreasing the water vapour partial pressure from 150 mbar to 10 mbar delayed the initiation of breakaway. This behaviour is consistent with observations previously reported.

The affect of increasing the Cr and Si content of the alloys on the resistance to oxidation has already been shown to have a dramatic effect (see Figure 13). Increasing the Si content in these alloys delays the onset of breakaway by preventing the chromium diffusion. This is achieved by the formation of SiO_2 at the metal/oxide interface, either as an internal oxide or as a continuous layer²⁶.

Murata *et al*²⁷ observed slower oxidation kinetics in alloys that had been produced with increased sulphur contents. Metallographic examination showed that sulphur was not incorporated into the oxide scale but instead concentrated ahead of the scale/substrate interface. This observation would imply that diffusion of sulphur ahead of the interface may become a rate-limiting step in the oxidation process. However it is possible that the high sulphur levels may increase the risk of scale spallation during thermal cycling.

For this class of materials it would appear that one of the major factors influencing the resistance to steam oxidation is the type of alloying addition. Much of the literature reviewed has focused on this and compared the relative resistance of alloys containing differing additions. Additions of Si, Ti and Y have been observed to improve the steam oxidation resistance whilst small additions of Ni reduce the resistance. It is important when considering alloying additions to maintain a global perspective of the balance between the mechanical properties and the corrosion resistance of the alloys, for example increasing the Ni content will decrease the creep resistance and increasing the Si content may lead to heterogeneous microstructures.

5 Austenitic Steels

Austenitic steels are more expensive than corresponding ferritic steels and have greater coefficients of thermal expansion and relatively poor thermal conductivity. Consequently applications for austenitic steels are restricted to the higher temperature boiler tubes i.e. superheaters and reheaters and to specific situations where severe corrosion conditions occur, e.g. in black liquor units. Austenitic materials are often used as weld overlay on ferritic materials to repair corroded areas or to provide protection in areas where corrosion could be a problem.

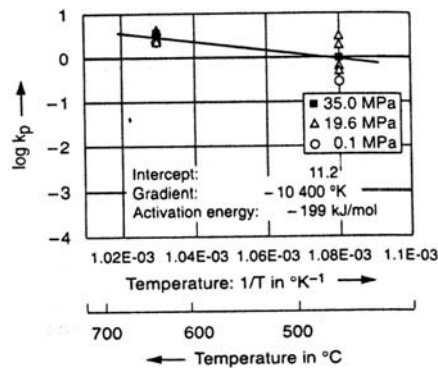
Key requirements are:

- Low costs
- Good fabricability
- Resistance to alkali salt corrosion
- Weldability

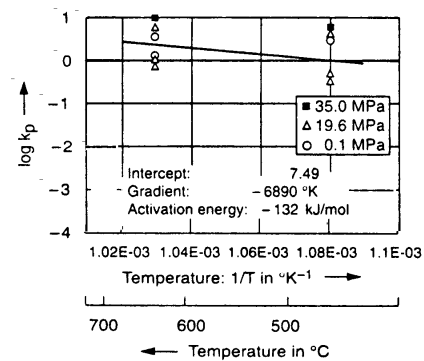
The philosophy behind the alloy development was to increase the volume fraction of strengthening precipitates by replacing chromium carbides with other more stable carbides, while at the same time freeing chromium back to the matrix to give improved corrosion resistance. The composition and mechanical properties of several common alloys are given in Table IX.

Table IX Composition of Austenitic Steels

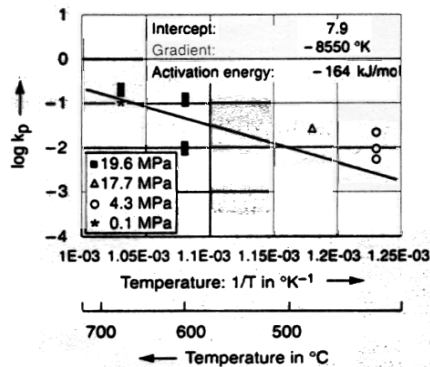
Alloy	Alternative nomenclature	Composition, wt%										Other
		C	Mn Max	P max	S max	Si max	Cr	Mo	N	Nb	Ni	
AISI 302		0.15	2	0.045	0.03	1	18				9	
AISI 304		0.08	2	0.045	0.03	1	18				8	
AISI 321		0.08	2	0.045	0.03	1	17				11	0.15 Ti
AISI 347		0.08	2	0.045	0.03	1	17				11	0.8 Nb+Ta
AISI 316		0.08	2	0.045	0.03	1	17	2.5			12	
AISI 309		0.2	2	0.045	0.03	1	23				14	
AISI 310		0.25	2	0.045	0.03	1.5	24				19	
ASME TP347HFG		0.08	1.6			0.6	18			0.8	10	
Tempaloy A-1	SUS321J1HTB	0.12	1.6			0.6	18			0.1	10	0.08 Ti
Tempaloy A-3	SUS309J4HTB	0.05	1.5			0.4	22		0.15	0.7	15	0.002 B
Super304H	SUS304J1HTB	0.1	0.8			0.2	18		0.1	0.4	9	3.0 Cu
HR3C	SUS310J1TB	0.06	1.2			0.4	25		0.2	0.45	20	
HR6W		0.10	2.0	0.03	0.03	1.0	23			0.4 max	40	6.0 W, 0.2 max Ti
NF709	SUS310J2TB	0.15	1			0.5	20	1.5		0.2	25	0.1 Ti
Esshete 1250		0.09	6	0.03	0.003	0.6	15	1	0.04		10	0.004 B, 0.02 Al, 0.9 Nb, 0.25 V, 0.14 Cu



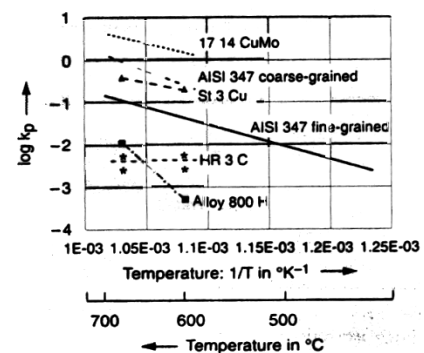
(a)



(b)



(c)



(d)

Figure 15 Arrhenius plots of steam oxidation constants for (a) 1714CuMo, (b) AISI347 (coarsed grained), (c) AISI347 (fine grained), (d) comparison of all the previous materials. Composition presented in Table X. (after Ref. 12)

Austenitic steels are used in many areas, which are subjected to varying temperatures and temperature gradients. Given that these materials generally have low thermal conductivities and high coefficients of thermal expansion, high thermal stresses can develop resulting in fatigue cracking²⁸. The high coefficients of expansion contribute to oxide scale spallation of austenitic alloys. Research during the last decade has generally focussed on developing high strength ferritic steels that can be used instead of the austenitic steels. This has led to the development of cost effective ferritic steels capable of operating in conditions up to 620 °C, whilst still exhibiting good weldability and fracture toughness. However, there is still a place for these austenitic materials that are primarily used in the finishing stages of SH/RH tubing, where oxidation resistance and creep resistance become more important.

Arrhenius plots, similar to those presented earlier for the ferritic steels, are presented in Figure 15. Plot (d) clearly shows the general trend for lower rate constants with increasing Cr levels in the alloys, as previously discussed. If the different alloys are compared it can be seen that all exhibit parabolic behaviour apart from HR3C. Montgomery¹² comments that it is difficult to compare data generated over widely differing time periods owing to the observed fact that parabolic rate constants are generally higher for short term tests than long term. This is a further difficulty encountered when comparing data from literature sources. Otoguro *et al*²⁹ conducted steam exposure tests on 4 steels, shown in Table X. The tests were fairly short term with exposures of 500 h, at temperatures of 700 and 650 °C, and steam pressures of 0.98, 19.6 and 34.3 MPa. Oxidation was measured by mass change.

Table X Chemical compositions of steels used by Otoguro *et al*²⁹

Alloy		Composition (wt%)								
		C	Ni	Cr	Mo	Ti	Nb	B	N	Cu
A	SUS 347HTB	0.07	11.3	17.8	-	-	0.72	-	0.01	-
B	17-14CuMo	0.11	14.5	15.9	2.50	0.24	0.43	-	0.01	3.1
C	20-Cr-25Ni type	0.07	25.2	20.1	1.56	0.06	0.27	0.004	0.18	-
D	22Cr-35Ni type	0.08	33.7	22.1	1.46	0.12	0.19	0.005	0.03	-

Calculations based on the assumption of formation of Cr₂O₃, Fe₃O₄ and FeO were made and the experimental data compared to predicted values. It was reported²⁹ that alloys C and D fall very close to the theoretical line, which corresponded to light spalling, A and B deviate far from them indicating heavier spallation, as shown in Figure 16. This figure shows theoretical predictions between mass gain from oxidation and mass loss from descaling. Otoguro *et al*²⁹ noted that the resistance to steam oxidation was influenced by four factors; steam pressure, temperature, Cr content and Ni content. Montgomery *et al*¹² suggest that by increasing the pressure you can increase the oxidation rate by decreasing the integrity of the scale. This has the secondary affect of increasing the oxidation rate by increasing the temperature of the underlying metal substrate. The effect of pressure is illustrated in Figure 17. Under high steam pressure, voids and cavities were found to have formed in the outer scale layer. It is claimed that this is attributed to the local cessation of the scale growth, the difference in the diffusion rates of the metallic ions in the outer and inner scale, and/or a weakening of the oxide grain boundaries²⁹.

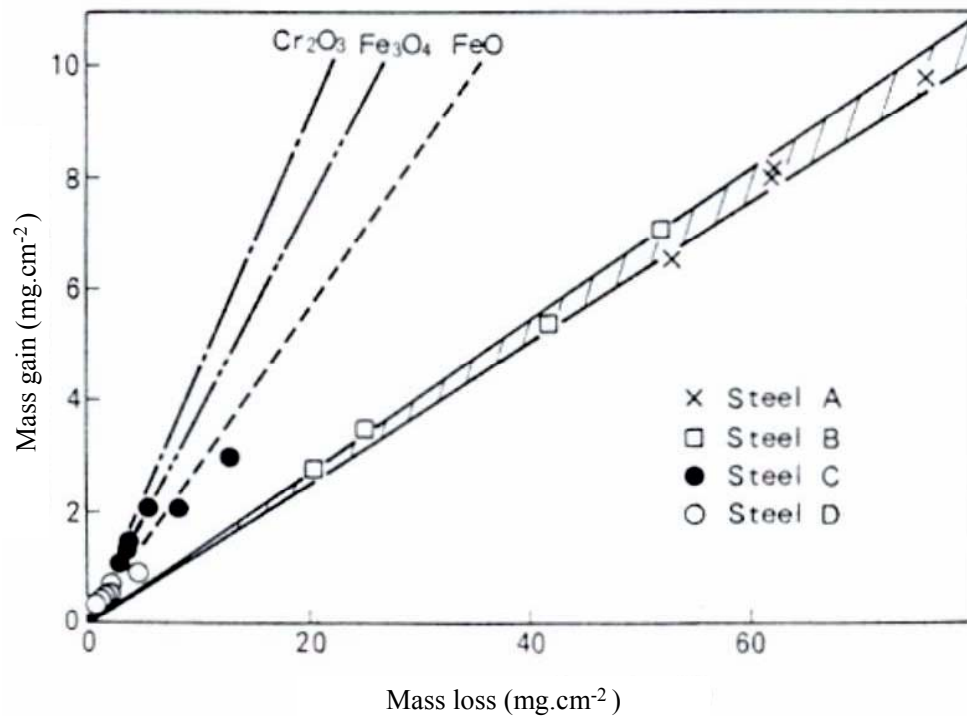


Figure 16 Weight loss and gain for the steels tested by Otoguro *et al* (after Ref. 29). Steel compositions are shown in Table X.

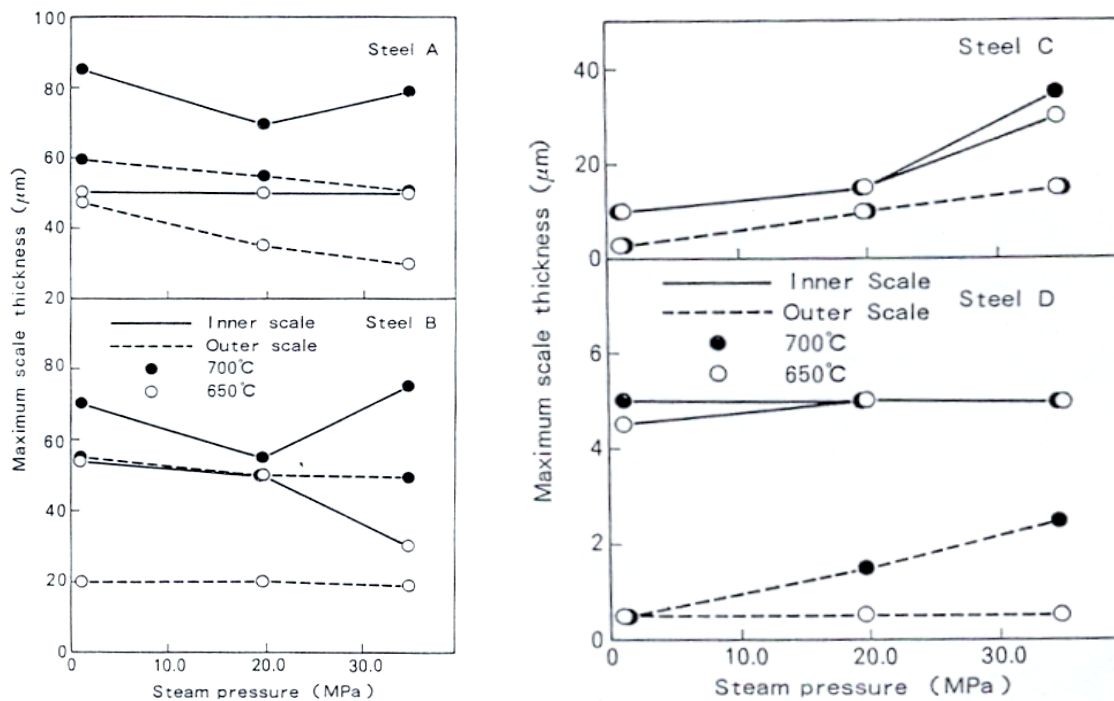


Figure 17 Relationship between steam pressure and maximum scale thickness of steels A, B, C and D from work conducted by Otoguro *et al*²⁹. Steel compositions are shown in Table X.

The gas velocity has been shown to strongly affect the oxidation of austenitic and ferritic chromium steels. In work conducted by Asteman *et al* ³⁰ it was concluded that the vaporization of chromium from the oxide in the form of chromium (VI) oxyhydroxide increased the oxidation rate of X20, 304L and 310 steels in O_2/H_2O environments. They found that at low gas velocities the X20 and 310 showed completely protective behaviour. In contrast the 304L material did not form a completely protective oxide at low gas velocities. For higher gas velocities (>2.5 cm/s), X20 exhibited breakaway corrosion while the oxide on the 304L and 310 was observed to fail locally. The effect of evaporation is schematically illustrated in Figure 18.

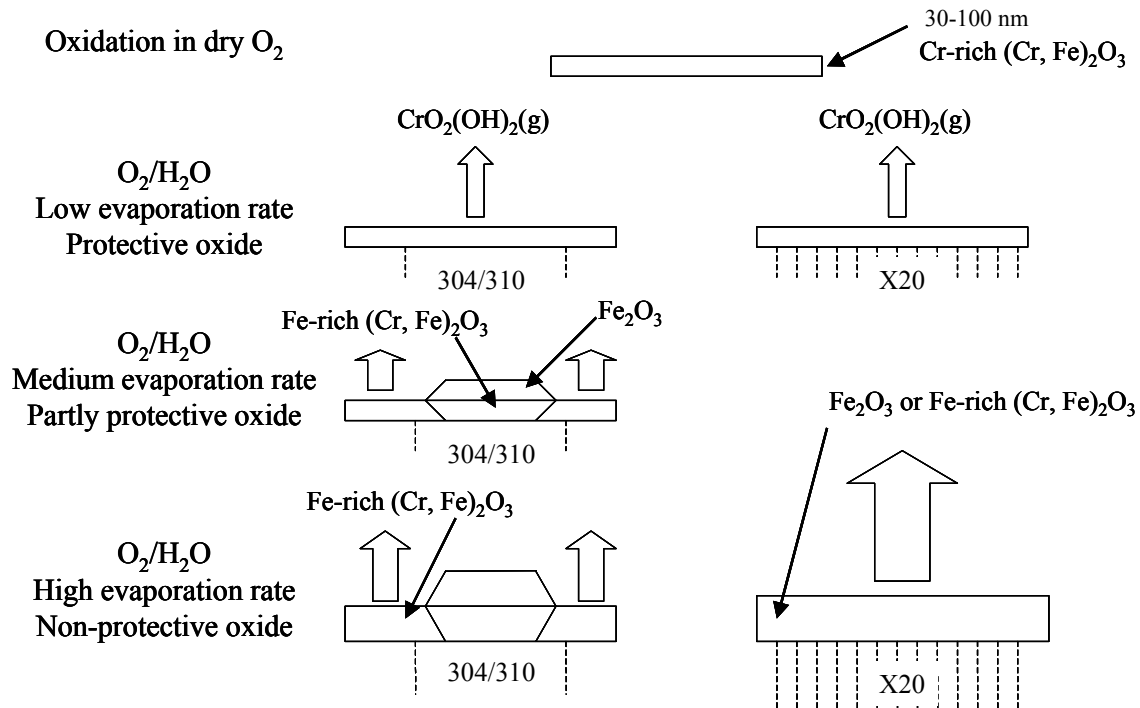


Figure 18 Schematic illustration of the oxidation of austenitic and ferritic chromium steels in O_2/H_2O environments. The illustration represents the situation after 168 hours as reported by Ref. 30

Whilst it is generally accepted that steels containing high levels of Cr have better corrosion resistance, it was observed by Otoguro *et al* ²⁹ that the weight loss in alloy B is less than that of alloy A in spite of lower Cr content, as shown in Figure 19. The authors suggest that this improvement in steam oxidation is caused by the higher Ni content. The benefit of Ni additions was also reported by Croll and Wallwork ³¹ who demonstrated the benefit on the oxidation resistance in Fe-Cr-Ni alloys. Caplan and Cohen ³² also showed that Ni increased oxidation resistance of stainless steels in wet air. It is suggested that this is due to the formation of a Ni enriched layer. As with martensitic alloys it has also been demonstrated that Si plays an important role in enhancing the oxidation resistance of austenitic steels by forming an inner layer of silica between the oxide scale and the alloys by promoting the rapid formation of Cr_2O_3 . This layer of silica, which grows much more slowly than chromia, acts as a diffusion barrier thus controlling the transport of Cr ions ³³. Chromium consumption decreases as a result and the depleted zone forms more slowly. Silica, it is claimed, also decreases the activity of Fe at the interface ³³.

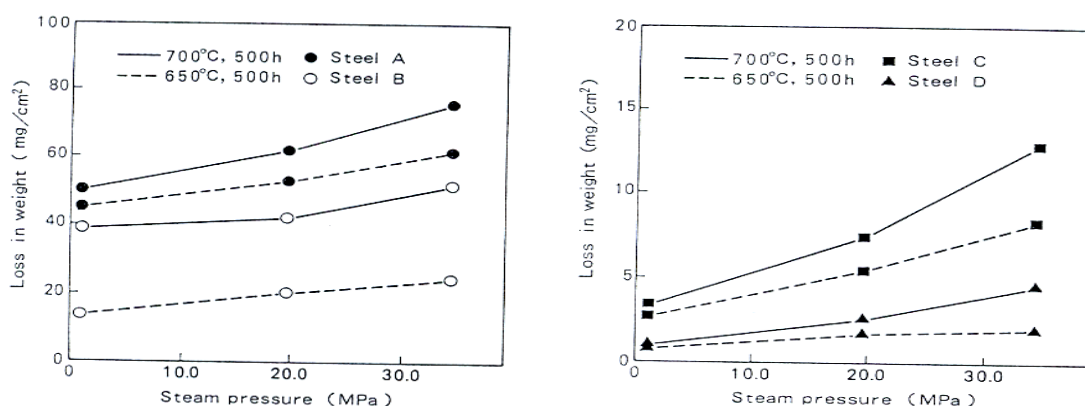


Figure 19 Effect of steam pressure on loss in weight for steels tested by Otoguro *et al*²⁹

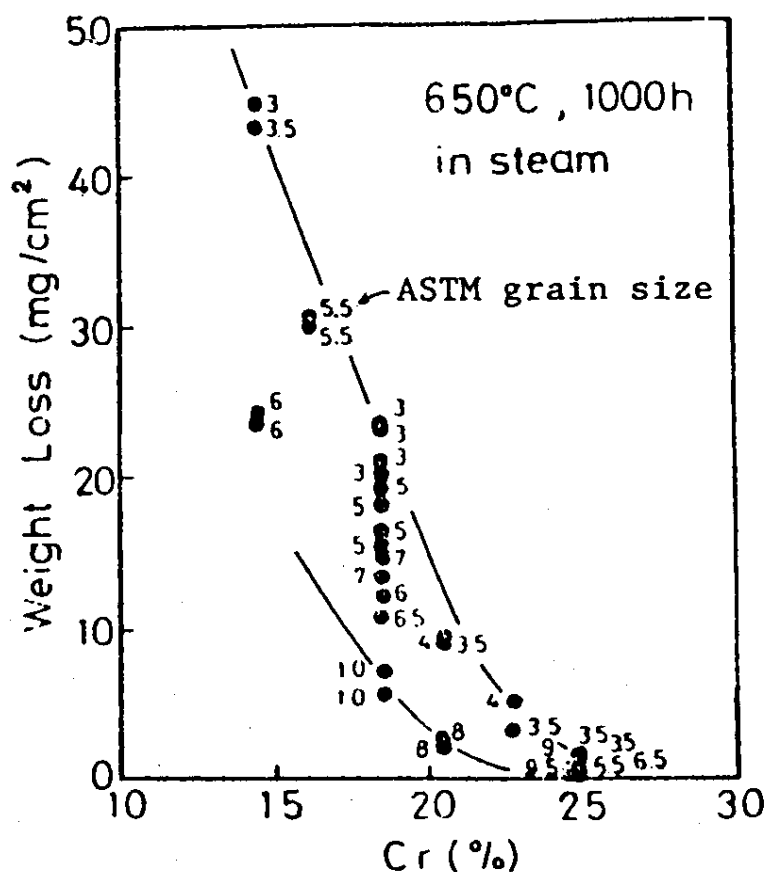


Figure 20 Effects of Cr content and grain size of austenitic stainless steel on steam oxidation (after Ref. 34)

There has been little investigative work into the comparative effect of the grain sizes within the base metal and the effect this has on steam oxidation. Although it has been reported by Teranishi³⁵⁻³⁶ that there is a marked improvement in the corrosion resistance of fine grained (ASTM 10), AISI 347, compared to a coarse grained (ASTM 3) version of the alloy. It is

suggested that even with a low Cr content alloy, a protective chromium oxide layer can be obtained through a finer grain size ²⁹. Figure 20 shows some comparative data reported in an EPRI report ³⁴ showing the affect of the grain size and Cr content for austenitic stainless steel in steam at 650 °C for 1000 h. Ootoguro ²⁹ also observed such behaviour in his studies. This effect is likely to be due to faster diffusion of Cr along the grain boundaries such that local depletion beneath the oxide scale does not occur.

The exposure technique can have a marked effect on the data obtained, as demonstrated with the lower Cr containing alloys. In work carried out by Griess and Maxwell ⁷, as discussed previously, samples of alloy 800, alloy 617 and Type 304 stainless steel were exposed to actual plant steam. The compositions of the alloys are given in Table XI. They claim that in the case of the Alloy 800 and the 304 stainless steel initial kinetics followed a parabolic growth rate until about 7000 hours followed by a shift to more linear oxidation kinetics, as previously exhibited by the 2¼Cr-1 Mo specimens. Although the oxidation kinetics exhibited the same pattern, the degree of oxidation was much lower, as would be expected because of the increased Cr content. Figure 21 shows the weight gain plots for Alloy 800 and the 304 stainless steel samples.

Table XI Composition of test materials (After Ref. 7)

Alloy	Composition (wt%)							
	C	Cr	Ni	Mo	Fe	Mn	Si	Other
Alloy 800	0.08	20.78	33.90		43.46			0.44 Ti, 0.46 Al
Alloy 617	0.07	20.30	57.35	8.58	1.01	0.05	0.16	11.72 Co, 0.76 Al
304 stainless steel	0.06	18.04	8.90		Bal.	1.84	0.55	

Surface preparation is a further factor that will influence the oxidation rate of a material. In the case of the Alloy 800 samples half were solution annealed at 1177 °C for 30 minutes in argon and air cooled and then pickled in HNO₃-HF, the other half were tested as ground without being heat-treated. It is immediately apparent that the ground sample oxidised at a very low rate. From further study of the pickled samples it was noted that they had apparently been sensitised during the cooling process and subsequently corroded intergranularly during the pickling process. The depth of the grain boundary penetration produced by pickling was about 200 µm, it is reported that this depth did not increase as a result of steam exposure. It is clear that care should be taken when performing surface treatments as it is established that ground surfaces of alloy 800 corrode less in steam than annealed ones, other alloys may adhere to this observation.

All of the 304 stainless steel samples were annealed and pickled, and then ground. There was no evidence of the sensitising effect as seen with alloy 800. The penetrations and corrosion rates were small when compared with the ferritic steels that were also tested. The growth of oxides scales on Cr-Mo steels and the austenitic stainless alloys is generally considered to be from both outward migration of iron ions to the surface, where they react with water molecules, and the inward diffusion of oxygen ions to the metal-oxide interface, where they react with the metal ³⁷. No explanation for the change from parabolic to a linear (Figure 21) rate was offered by the authors for the previous work.

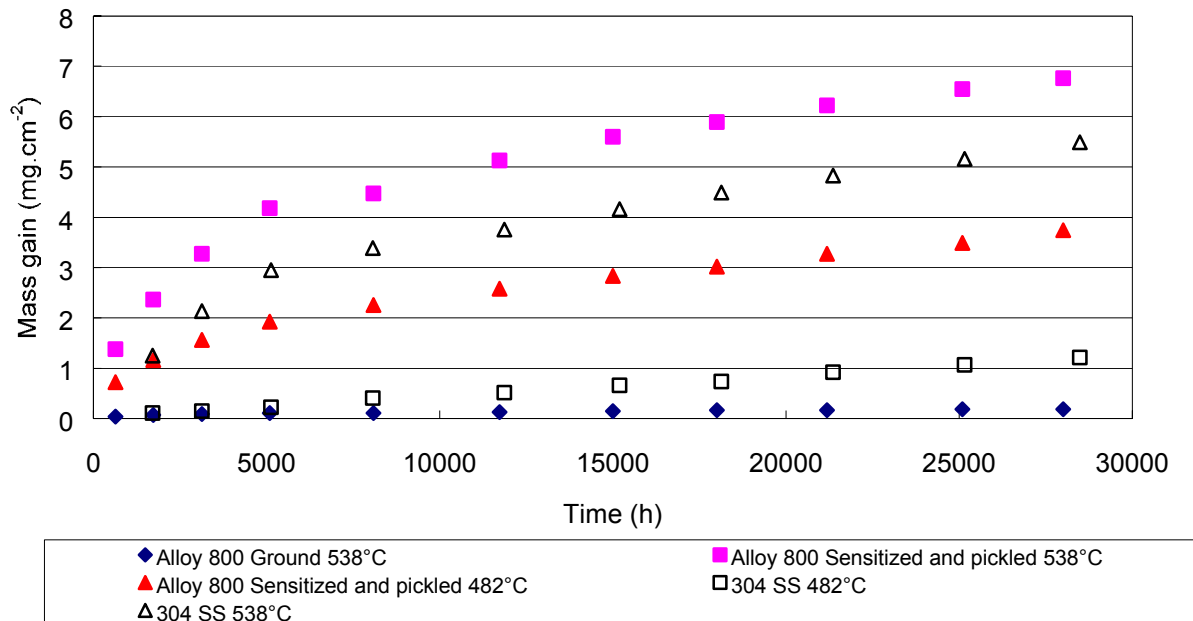


Figure 21 Mass gains for alloy 800 and 304 Stainless Steel in superheated steam (after Ref. 7)

From the literature two main points are clear regarding this class of material, namely that the oxidation rate increases with high pressure atmospheres and that fine grain sizes improve the oxidation resistance by supplying Cr to the surface.

6 Ni- and Co-based alloys

Ni- and Co-based alloys are used for “hot-end” parts in gas turbines and although there are some other minor applications, it is the requirements defined for gas turbines that drive developments. In the absence of improved materials the only option open to the design engineer faced with developing engines with greater performance is to design improved cooling technologies. The key property requirements are indicated below.

Blades and Vanes:

- High creep strength at temperatures up to 1150 °C
- Good processability in single crystal and D.S. forms to ensure high casting yields to reduce costs
- Thin-wall castings with high strength
- High thermo-mechanical fatigue (TMF) resistance
- Adherent oxide layer for good oxidation resistance
- Resistance to hot salt corrosion

Discs:

- Uniform grain structure (processing of large forgings)
- Fracture toughness and resistance to fatigue crack initiation and growth
- Low Cycle Fatigue resistance
- Resistance to SAGBO

Combustors:

- Increased temperature capability
- Weldability and formability
- Low Cycle Fatigue resistance
- Good repairability

Care should be exercised when testing this class of materials as the environmental conditions, primarily the presence of oxygen and/or moisture in the test environments, have been observed to have significant effects ³⁸.

Commonly coatings are used to confer corrosion resistance. Nonetheless corrosion resistant alloys have been developed where generally a higher Cr/Al ratio is required than alloys developed purely for creep resistance. Mo which was present as a solid solution strengthening element has poor hot corrosion performance and this is normally replaced by refractory element such as W, Ta and Nb ³⁹.

Although quite a widely used class of material, very little information is available in the open literature regarding the steam oxidation behaviour. Exposures in different forms of steam, that is flowing plant, static etc, have been reported in work previously discussed in the earlier sections. Thus Griess and Maxwell ⁷ exposed samples of Alloy 617 to plant steam. Very little corrosion occurred during the test, although for Ni-based alloys the temperature was low (482 and 538 °C). The oxide layer formed on the samples was so thin that it was claimed to be undetectable at a magnification of 500x. The composition of the alloy is presented in Table XII.

Table XII Composition of materials

Alloy	Composition (wt%)								
	C	Cr	Ni	Co	Mo	Fe	Mn	Si	Other
Alloy 617	0.07	20.30	57.35	11.72	8.58	1.01	0.05	0.16	0.76 Al
Incoloy 800	0.04	20.0	33.0			45.2	0.85	0.40	0.007 S, 0.41 Cu
Inconel 600	0.04	16.3	75.9			7.24	0.17	0.29	0.007 S
Inconel 625	0.03	22.0	62.3		8.75	1.86	0.12	0.25	0.17 Al, 0.007 S [(Cb + Ta) 4.24, Ti] 0.23
Inconel X750	0.04	15.13	72.5			6.87	0.45	0.25	0.74 Al, 0.007S (Cb + Ta) 0.98, Ti 2.62
Rene 41	0.07	19.05	55.02	10.95	9.83	0.3		0.05	1.52 Al, 3.21 Ti

In much older work conducted by Ruther and Greenberg⁴⁰ a number of alloys were tested at 650 °C in static autoclaves for short durations. The results of these tests are presented in Figure 22. Results from earlier corrosion tests on type 304 and 406 steel have been included to establish reference levels. Of the Ni-based alloys tested Inconel 600 and Inconel X750 (Inconel X in Figure 22) offered the weakest corrosion resistance. The three remaining alloys all showed metal losses less than type 406 (reference line shown in Figure 22) for exposures up to 56 days (1344 hours).

It has been demonstrated in earlier sections that the surface preparation can influence the oxidation kinetics in steam exposures. This class of alloy has also been observed to display this effect. Incoloy 800 is reported to have exhibited a strong surface preparation effect. The metal loss increased from 0.13 to 4.67 mg.cm⁻² when the surface was electro-polished as opposed to being just wet ground. Jansson *et al*⁴¹ have conducted further investigations concerning the effect of surface preparation, comparing ground surfaces with pickled ones. They found that ground surfaces exhibited lower mass gain than pickled ones for all the alloys they tested up to 650 °C. The beneficial effect of grinding was found to decrease with increasing temperature up to 800 °C, the retardation caused by grinding being reduced to a factor of 1-3. The results for an alloy with nominal composition of 16% Cr and 75% Ni are shown in Figure 23.

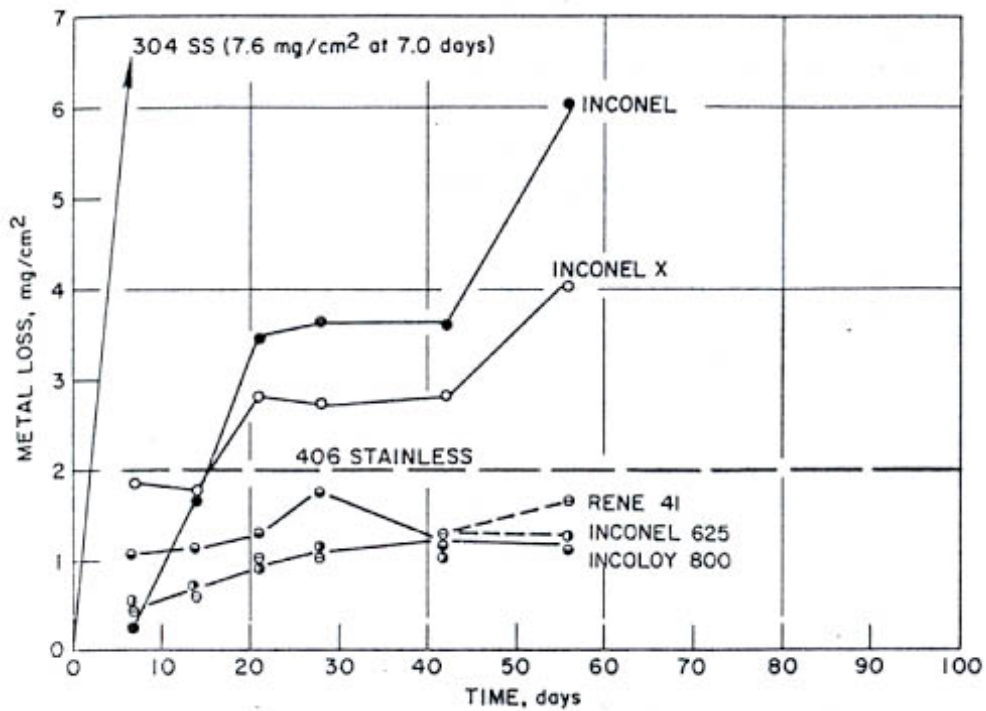
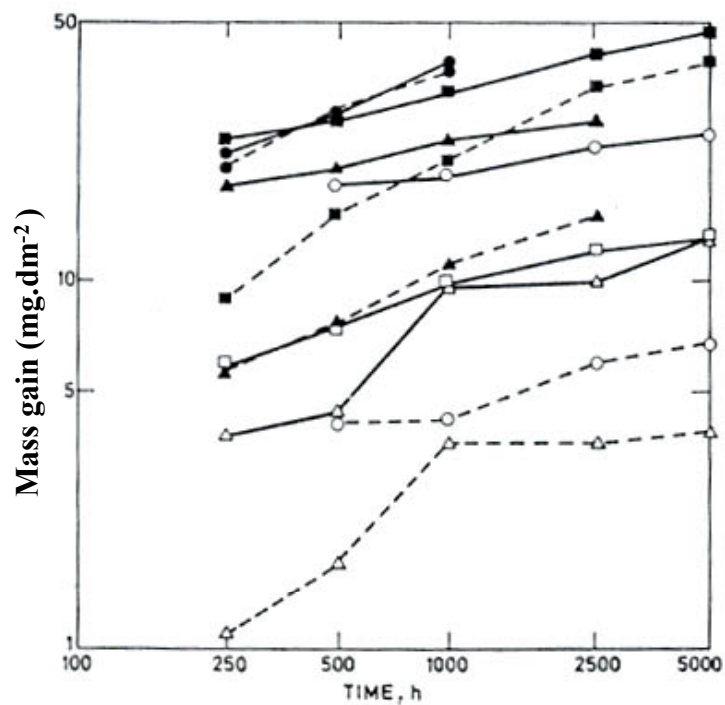


Figure 22 Corrosion of nickel alloys in flowing steam; 650°C , $42 \text{ kg}/\text{cm}^2$, 61 m/s velocity, 30 ppm oxygen (after Ref. 40)



Mass gain of 1675 in steam with low oxygen content

— Pickled; - - - ground
 Δ 500°C; $\square$ 550°C; $\circ$ 600°C; $\blacktriangle$ 650°C; $\blacksquare$ 700°C; $\bullet$ 800°C

Figure 23 Mass gain results of a Ni-base Alloy (after Ref. 41)

The improvement bestowed by grinding can be explained in the following way. The grinding process, it is suggested, causes a high density of dislocations or sub-grain boundaries, these in turn provide chromium enhanced diffusion paths, which leads to a higher level of chromium in the metal layer beneath the oxide, thus imparting greater protection to the base metal. The absence of this retarding effect at the higher temperatures is a consequence of recovery and recrystallisation of the surface structure. It was also observed that increasing the oxygen content of the steam caused the retarding effect of grinding to diminish.

One of the main difficulties in reviewing the steam oxidation characteristics of this class of material has been the lack of information openly available with the literature, although some interesting points have been highlighted above.

7 Mechanisms of Oxidation Under Environments Containing Water Vapour

It is well known that the oxidation behaviour of alloys in environments that contain water vapour differs strongly from that in 'dry' atmospheres e.g. oxygen or air. However there is still not a complete understanding of the mechanisms behind these observations.

There are five main mechanisms commonly used to account for the effect of water vapour on oxidation kinetics. They are⁴⁶:

- Dissociation mechanism
- Oxidant-gas penetration mechanism
- Formation and volatilisation of $\text{Fe}(\text{OH})_2$
- Formation and volatilisation of $\text{CrO}_2(\text{OH})_2$
- Changes in the oxide defect structure via proton dissolution

7.1 Dissociation Mechanism

The dissociation mechanism, proposed by Fujii and Meussner⁴⁷⁻⁴⁸, is illustrated in Figure 24. Metal ions that are generated from reactions at interfaces (2) and (4), migrate to the outer interface of the oxide scale and the atmosphere (1), where water vapour is adsorbed. The subsequent reaction forms wustite, defects in the oxide and adsorbed hydrogen. Most of the hydrogen is believed to desorb, but some will dissolve in the oxide.

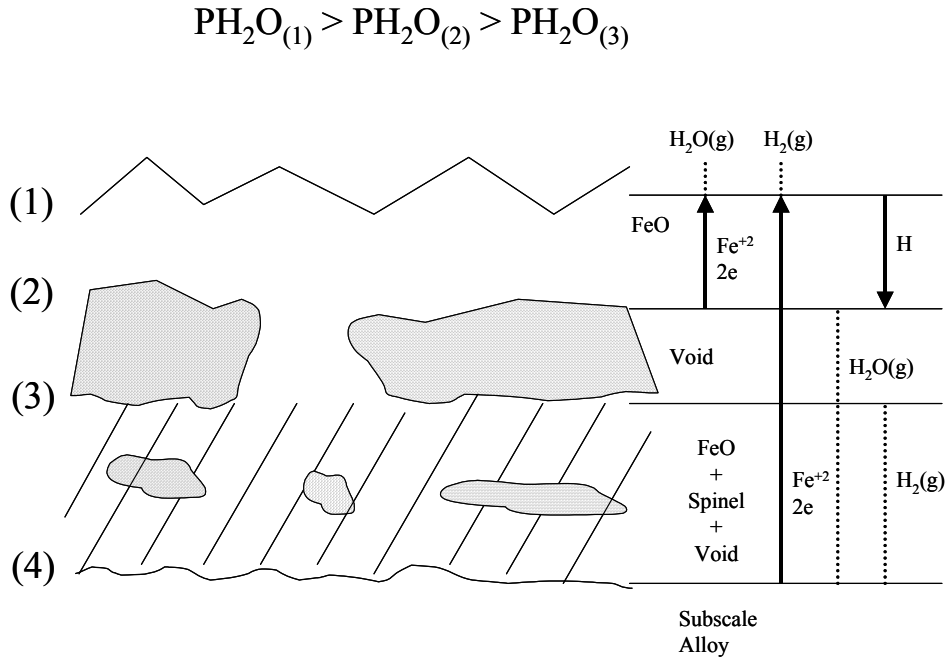
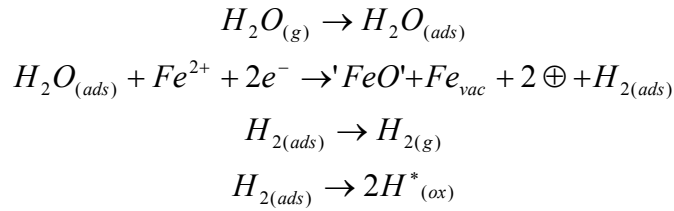


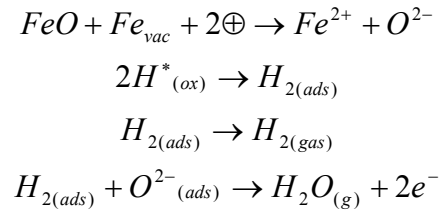
Figure 24 Dissociation mechanism proposed by Fujii and Meussner (after Ref. 46)

At interface (1) the reactions are proposed to be as follows,

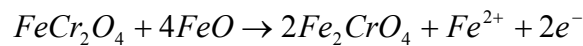


where Fe_{vac} indicates a vacant iron ion site and $\oplus$ is an electron defect, H^* represents hydrogen dissolved within the oxide.

The iron oxide at interface (2) is believed to dissociate and produce an oxide ion as an adsorbed species. The permeating hydrogen permits these adsorbed species to react to form the carrier gas for oxygen transport to the void, as follows,



Wustite layers of the outer scale are formed in this resultant atmosphere by the reaction as defined for the interfaces (1) and (2). In this way reactions similar to those found at (1) also occur at interface (3). The composition of the spinel phase is believed to be altered, such that,



This mechanism for the formation of an inner scale was proposed after studies on the oxidation of Fe-Cr alloys (0-25% Cr), which were conducted in Ar10%H₂O over a temperature range of 700-1100 °C. Scales consisting of three distinct zones were observed, an outer zone composed of one or more layers of wustite, an inner porous scale containing wustite and an iron-chromium spinel-oxide, and a subscale of iron-chromium spinel ⁴⁶.

7.2 Oxidant-gas Penetration Mechanism

In oxidation studies conducted by Ikeda and Nii ⁴⁹⁻⁵⁰ on Fe-Cr alloys (5-30%Cr) in dry oxygen and in O₂-10% H₂O at 750 °C and 900 °C, it was observed that alloys with chromium content greater than 15% had a mass gain an order of magnitude greater in wet oxygen than in dry oxygen. Two possible reaction mechanism were compared, i.e. the dissociation mechanism (Section 7.1 above) and oxidant-gas penetration. The authors showed by simple gas kinetics based calculations that the dissociation mechanism was not an appropriate explanation, and thus proposed the oxidant-gas penetration mechanism. This basically states that via the development of microcracks and pores in the scale, oxygen and water vapour can pass directly to the metal surface, assuming the size and frequency of the cracking is large. Further calculations by Honda *et al* ⁵¹ have confirmed that the supply of oxygen via water vapour was faster than in dry atmospheres, although it was still insufficient to account for all the observed weight gains – thus causing further doubt regarding the dissociation mechanism.

Oxidation would proceed in the following manner. Initially a chromia layer would cover the alloy surface. Gas penetrating through a crack or pore into a void could increase the partial pressure of oxygen within the void in such a way that the iron is oxidized. The resultant mixed-oxide scale would not be able to prevent outward diffusion of iron ions, and so an iron-rich outer scale is likely to form. The presence of these microcracks or pores was confirmed by sulphur decoration.

Ikeda and Nii ⁵⁰ observed that under dry oxygen conditions the gas penetration was infrequent, while in wet oxygen conditions it was always observed. It was suggested that the water vapour caused more frequent scale cracking and also prevented the scale from healing, thereby accelerating the oxidation process.

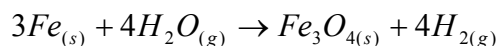
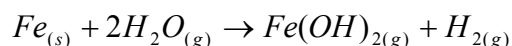
7.3 Formation and Volatilisation of Fe(OH)₂

Surman and Castle ⁵²⁻⁵³ proposed a mechanism based on formation and volatilisation of Fe(OH)₂ to account for the accelerated oxidation of chromium steels in the presence of water vapour. They suggested that the rate-determining step could be one of three things –

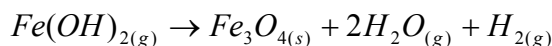
- Outward diffusion of iron cations to the oxide/gas interface
- Inward diffusion of oxygen anions to the metal/oxide interface
- Vapour-phase diffusion of Fe(OH)₂ to the oxide/gas interface

The model that they used assumed the following phase boundary reactions for the formation and dissociation of the volatile hydroxide.

Metal/oxide interface,



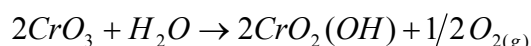
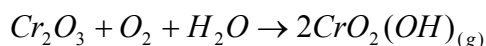
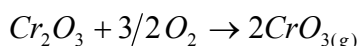
Oxide/gas interface,



For each of the three mechanisms, comparisons were made between the experimental value for the temperature dependence of the parabolic rate constant and that of the theoretical value. The theoretical value for the vapour phase diffusion model gave the best fit and was considered the most likely mechanism, although quantitatively the predicted rate constants are over an order of magnitude too low. This mechanism has also been cited by other workers⁵⁴⁻⁵⁵, whilst Klein *et al*⁵⁶ have disputed the validity of Surman and Castle's work. The main objection was that in steels containing nickel and cobalt the outer oxide layers did not contain either of these elements although the volatility of nickel and cobalt hydroxide is similar to iron hydroxide.

7.4 Formation and Volatilisation of $CrO_2(OH)_2$

This mechanism would suggest that the evaporation of volatile chromium species primarily along the grain boundaries accounts for scale cracking and spallation of oxide scales in the presence of water vapour. Armanet *et al*⁵⁷ exposed a selection of alloys to pure oxygen, air and wet air. They found that the oxidation of Ni-20Cr in both dry air and wet air resulted in the formation of three oxides. These were Cr_2O_3 , NiO and the spinel oxide $NiCr_2O_4$. Whilst in the dry air the NiO phase gradually disappeared with time by reaction with chromia to generate the spinel, in the wet atmosphere, the NiO persisted. Significant cracking and spallation is reported to have occurred. It is suggested that during volatilisation compounds rich in chromium would exert an over-pressure, which would cause the oxide layer to burst. When the chromia-layer was continuous at the alloy/oxide interface, compressive stresses would be induced causing breakdown of the NiO and $NiCr_2O_4$ layers. The chromia layer is then in contact with the atmosphere and would volatilise as CrO_3 and $CrO_2(OH)$. The alloy now depleted in chromium would reoxidise and a new layer of NiO, and eventually spinel, would develop. This process would continue in such a manner so that the steady state seen during dry oxidation would not be attained.



7.5 Changes in the Oxide Defect Structure via Proton Dissolution

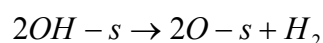
Water vapour may have an effect on the defect structure and defect-dependant properties of many oxide systems. It is suggested that water vapour serves as a source of hydrogen, which

dissolves as protons in the metal oxide. Also water vapour may affect the majority-defect dominated properties such as diffusion-controlled transport of reactants through growing scales, or minority dominated defects such as high temperature creep.

Galerie *et al*⁵⁸ have compared the oxidation of metals in oxygen and in water vapour. Two main areas of interest were identified; these were the nature and effect of the major point defects in the oxide, and the effect that the acidity of the oxide surface had.

In examining the nature of the point defects, Galerie *et al* considered point defects such as substitutional sites and interstitial sites and grain boundary defects. Water vapour was considered to enhance the oxidation of metals. That is provided that oxygen was among the most mobile species in the formed oxide. The solubility of hydrogen in the metallic substrate was also deemed to be of importance, since metals that were most affected by the water vapour were those that exhibited hydrogen solubility.

The rate-controlling step in oxidation is the transport of oxygen through the oxide via hydroxyl defects. This being the case, it is likely that the generation of OH species on the oxide surface is also a very important factor. Indeed water adsorption studies⁵⁹⁻⁶¹ have shown that an oxide surface exposed to steam is easily covered with hydroxyl species, but oxygen species are much more difficult to form. To form oxygen species the surface must fix the OH particle by its oxygen electron pairs, which leads to a high polarization effect thereby promoting the disassociation of the second O-H bond. To achieve this the surface must exhibit acidic properties. Galerie *et al*⁵⁸ have shown that pure metal species that did not have acidic oxides had very slow oxidation rates in water vapour compared to oxygen. In these circumstances it is suggested that the oxidation rate is controlled by the decomposition of OH species in the absorbed phase as shown below:



where s is an adsorption site on the oxide surface. This would yield a linear rate law and thus the effect of the water vapour pressure would follow:

$$r = k[\theta]^2$$

where r is the reaction rate, k the rate constant and θ the fraction of the oxide surface covered by OH species, this is given by Langmuir's equilibrium equation:

$$\theta = \frac{KP}{1 + KP}$$

where P and K are the water vapour pressure and equilibrium constants, thus

$$r = k \left(\frac{KP}{1 + KP} \right)^2$$

In the case of acidic oxides Galerie *et al* report that the rate of OH surface decomposition was high enough to supply oxide ions to the scale as rapidly as they were being consumed, and the reaction rate was not limited by the decomposition. A general rule is proposed: "Water vapour may react more rapidly with metals than oxygen provided that the formed oxide can

grow by transport of hydroxyl ions. If this is not possible, the rate of the reaction will depend on the surface acidity of the oxide, i.e. the lower the acidity – the slower the reaction”⁵⁸.

It is unclear as to which mechanism to prefer as none of the suggested mechanisms seem to adequately explain all of the observed behaviour.

8 Discussion and Conclusions

Although there is a large body of work concerned with oxidation in steam or high moisture, it is difficult to extract coherent themes even within a single alloy class. Galerie⁵⁸ suggested the major reasons behind this confusion as being:

- Within industrial situations actual pure water vapour, with a maximum oxygen partial pressure equal to its decomposition pressure, is seldom, if ever encountered.
- Atmospheres consisting of pure water vapour are very difficult to produce and maintain, thus reported observations within the literature are subject to caution.
- As a consequence of the two points already mentioned, much of the reported work deals with atmospheres consisting of O₂/H₂O, air/H₂O or H₂/H₂O mixtures.

The apparent lack of basic understanding of steam oxidation is understandable given the complexities encountered. Further work is required to enhance the current level of understanding, in particular the influence of laboratory test procedures on the resultant data. The precise in-service conditions are difficult if not impossible to reproduce in the laboratory and some degree of simplification is necessary. Several exposure procedures are in common use in the laboratory – in ascending order of complexity these are:

- Water vapour in a carrier gas (usually argon)
- Flowing steam at atmospheric pressure
- Static steam at high pressure
- Flowing steam at high pressure.

However, there is little evidence of comparisons between the different techniques. Such a comparison between the different methods with in-service exposure would be of great benefit to the industry as it would give clear guidance as to which method produces oxide scales which most closely resemble those seen from real exposures.

The review has also shown that subtle changes in the alloy composition can have marked effects on oxidation resistance in steam atmospheres, for example the addition of Si or rare earth elements. Further investigation of the effects of alloy composition changes could be beneficial in terms of future alloy development and plant design.

In addition to these points it is important to remember that oxidation is a dynamic process, the presence of oxide scales will act to reduce the thermal diffusivity of components. Within the course of this review very little information regarding the thermal conductivity of components with oxide scales was apparent. Thus a further avenue of work to aid in the lifetime evaluation of components must include some activity on thermal conductivity

measurement of oxide scales as the scale grows. Data from such measurements would be an invaluable tool for modellers to use in the evaluation of component life.

The main points from the review are summarised below:

In general

- Increasing Cr content improves the steam oxidation resistance
- There is no consistent effect of steam pressure

For low alloy (1-3%Cr) steels

- Growth kinetics are affected by the flow rate of the steam atmosphere
- Growth kinetics range from sub parabolic at low temperature (500 °C) to approaching linear at 650 °C
- The presence of water vapour in the test atmosphere may increase or decrease corrosion rate, depending on test temperature

For martensitic (9-12%Cr) steels

- Additions of Si, Ti and Y improve the steam oxidation resistance
- The addition of small (<1%) amounts of nickel reduces steam oxidation resistance

For austenitic steels

- Oxidation rates increase under high pressure atmospheres
- Fine grain size improves oxidation resistance by increasing the supply of Cr to the surface

For Ni and Co base superalloys

- Little information exists in the published literature regarding the steam oxidation resistance of this class of alloy

In conclusion, this review has shown the need for a systematic study of the effects of alloy composition, laboratory test procedure and steam chemistry on steam oxidation behaviour. Critical tests are required to establish the mechanisms operating in the different alloys and whether these are affected by the experimental parameters. One possible route is through modelling and analysis of the steam atmosphere to determine the presence or otherwise of volatile species in the environment. Other critical measurements are the composition, microstructure and growth kinetics of the oxides that are formed as a function of exposure procedure and alloy composition.

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