

The oxidation behaviour of metals and alloys at high temperatures in atmospheres containing water vapour: A review

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Abstract

The kinetics of oxide formation in the presence of water vapour are discussed and compared with oxidation in dry atmospheres. The main protective oxide systems are considered, i.e. alumina, chromia, silica, titania and iron and nickel oxides, and with the possible exceptions of alumina and nickel oxide, oxidation rates are increased by the presence of water vapour. Scale morphology is also influenced by water vapour, and an important observation is that whisker formation is encouraged; this is believed to be due to the more rapid dissociation of water vapour compared to oxygen. In general, water vapour promotes the formation of a more porous scale. This is related to an increase in cation diffusion and consequent vacancy condensation, thereby developing a porous structure. The thermochemistry of oxide formation is discussed, and here oxide stability and hydroxide formation are considered. A significant observation is that where hydroxides or oxyhydroxides form, they generally have higher volatility than the corresponding oxide, and this leads to loss of protection.

The effect of water vapour on oxide growth processes is considered. It is demonstrated that all aspects of oxide growth including adsorption, dissociation and diffusion of reactants are altered in the presence of water vapour compared with similar processes in dry conditions. The important first stages of the reaction involving adsorption and dissociation are controlled by the catalytic activity and acid base nature of oxides. For oxides formed at high temperatures very limited information is available, but, in general, data obtained at room temperature is confirmed and strongly suggests that dissociation of any gas molecule is favoured by defects in the surface. Dissociation of water seems to be more rapid at lower temperatures than, for example, oxygen, but this difference may be less pronounced at higher temperatures. Fast diffusion of water in oxides is possible due to

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“proton hopping”, in which protons localised at oxide ions move by transfer from one oxygen to another. Since the OH^- ion concentration is increased there is a resultant increase in cation vacancies, and this, in part, is responsible for the observed increase in oxidation rates. A further factor to consider is the possibility of molecular diffusion, and it has been demonstrated that where pores or voids are present in the scale, and the void contains both hydrogen and water vapour, oxidation of the surface nearest the metal will occur by reaction with water to form new oxide and the reaction product hydrogen, while a reduction reaction occurs at the surface of the void nearest the gas phase to produce water vapour. Thus it can be seen that this process provides for rapid inward diffusion of oxygen while the void gradually moves outwards from the metal/oxide interface to the oxide/gas interface.

Finally, the review considers the effect of water vapour on the mechanical properties of the scale. Scale adhesion can be improved (iron oxides) or made worse (alumina and chromia) by the presence of water vapour. It is shown that while there is experimental evidence for altered mechanical behaviour, there is very little data on relevant mechanical properties. It is possible, therefore, that water vapour either alters mechanical properties of some oxides, or, as has been demonstrated, the oxide growth process has been changed. Alternatively, at least for the cases where increased oxidation rates were caused by the presence of water vapour, the observed differences between wet and dry behaviour may simply be a function of the greater scale thickness. A significant effort has been made to develop models that can be used to predict the onset scale spallation observed in industrial boilers using process steam. The further development of these models is strongly dependent upon obtaining relevant input data, and this is considered a major challenge for materials scientists.

Some areas for future research are proposed.

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1. Introduction

Water vapour is present in nearly all atmospheres where metallic materials are used at high temperatures for industrial processes and predominantly this relates to the power generation, petrochemical and aerospace sectors. The most extreme case relates to steam generators where the moisture content is 100% as found in power station boilers, and also in many other cases where heat recovery steam generators (HRSG) are used to either generate electrical power or to produce process steam. Combustion of fossil and bio-fuels (C_xH_y) produces atmospheres very rich in water vapour, typically about 7%² for coal combustion, but this will vary depending on the combustion conditions and fuel (coal, CH; oil, CH₂; and gas, CH₄). For example, in low NO_x conditions for coal combustion, i.e. fuel rich, a higher water vapour content is found. In stationary gas turbines, NO_x control is achieved by injection of steam to lower the flame temperature. Biomass although low in hydrogen (for example, 6% for wood) will contain 20–30% moisture after air drying [1]. The development of the solid oxide fuel cell (SOFC) has re-awakened interest in the effects of water vapour on high temperature oxidation. Here the interconnect material is required to be resistant to both reducing and oxidizing atmospheres both of which contain water vapour [2]. Many petrochemical processes involve the use of steam in reducing environments with high carbon activity and may also contain sulphur-containing gases. The process vessels or tubes are often fabricated from metallic materials and thus rely upon formation of a protective oxide layer, so that here too the effects of water vapour would be expected to be important. Finally, for the microelectronics industry, the oxidation of silicon to form silica is the basis of all integrated circuits, and this oxidation is normally carried out in dry oxygen or an oxygen/water vapour mixture.

Frequently, particularly for some older research, experiments were carried in uncontrolled laboratory air where the moisture content may have been as high as 3%. In such

² All gas compositions are quoted as volume% unless otherwise stated.

cases often no account was taken of the possible effects of water vapour on the rate of reaction or the resultant scale microstructure. Furthermore a large number of studies of the oxidation of metals and alloys have described results where the $p(\text{O}_2)$ was controlled by use of $\text{H}_2/\text{H}_2\text{O}$ mixtures. The effect of the presence of water vapour may have significantly affected the behaviour.

This review will consider the kinetics of oxide growth in the presence of water vapour. The main protective oxide systems will be discussed, alumina, chromia, and silica as well water vapour effects on titanium and its alloys and iron and nickel oxide. As will be seen, water vapour may also affect the mechanical properties of scales, thus this topic will also be considered. Finally an attempt is made to summarise the various ideas proposed in the literature to account for the observed effects. This will involve consideration of the thermochemistry of oxide formation (stability and volatility) in water vapour containing atmospheres, oxide microstructural development and transport processes in the growing oxide.

2. Kinetics effects

2.1. Alumina

There are conflicting reports about the effect of water vapour on the oxidation rate of alumina-forming alloys. A wide ranging review of the effects of water vapour on the oxidation of metals was completed in 1994 [3]. In general, it was concluded that water vapour had little effect on the oxidation of alumina-forming alloys, although some evidence was cited that hydrogen defects were present in Mg-doped aluminas and scale adhesion was reduced by water vapour. This conclusion has been generally confirmed in this review. The research of Buscail et al. [4] showed that the rate of oxidation of Fe, 21.5% Cr, 5.6% Al^3 was slightly reduced in oxygen 14.85% water vapour at 1000 °C compared with dry oxygen (Fig. 1). It was proposed that water vapour encouraged the formation of hexagonal oxides similar to the protective $\alpha\text{-Al}_2\text{O}_3$ that eventually forms, whereas in dry oxygen, the faster growing cubic $\gamma\text{-Al}_2\text{O}_3$ initially forms. It was also shown that the hexagonal alumina that formed in the early stages of oxidation in water vapour containing atmospheres contained minor amounts of Fe and Cr, and that in corrosion tests these scales were less protective than the α -alumina that developed in water vapour free atmospheres. Later work by Al-Badairy and Tatlock [5] demonstrated that for 125 μm thick PM 2000, a mechanically alloyed material (see Table 1 for composition)⁴ in air +2.5% H_2O at 1300 °C the growth rate is only slightly increased in isothermal oxidation by the presence of water vapour, and that the time to breakaway in cyclic tests was shorter for the atmospheres containing water vapour. In both cases the differences were ascribed to water vapour encouraging enhanced gaseous transport and hence early formation of the stable α -alumina. There was no difference in oxide microstructure and composition once a stable protective layer had formed, but the early breakaway was attributed to Al depletion effects in the thin substrate as a consequence of faster alumina growth. In older work Boggs [6] showed that the oxidation rate of Fe 5% Al was significantly increased at 800 °C when

³ All alloy compositions are quoted as mass% unless otherwise stated.

⁴ All other proprietary alloy compositions referred to in this review are also listed in Table 1, nickel-base alloys, and Table 2, iron-base alloys.

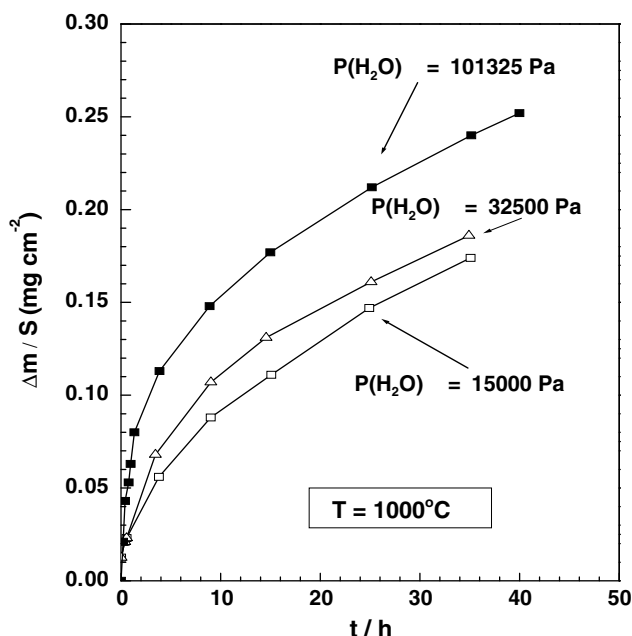


Fig. 1. Weight gain vs. time. water vapour-ratio effect on Kanthal-A1 oxidation at 1000 °C, after Ref. [4].

about 3% water was present either alone or with oxygen. γ -alumina formed initially in dry oxygen which later transformed to α -alumina, with about 1% iron-rich nodules forming after 16 h exposure, whereas in the wet atmosphere iron-rich nodules covered about 20% of the surface. It was proposed that a hydrated alumina may have formed in the early stages of growth in the wet atmosphere which was more susceptible to cracking and this led to the large increase in nodule formation.

Opan et al. [7] described the results of extensive cyclic oxidation tests on a number of Ni-base alumina-forming alloys (PWA 1484, CM 186, MarM 247 and Rene'N5) in the temperature range 700–1100 °C in air containing up to 30% water vapour. At temperatures of ≥ 900 °C water vapour had little effect on the oxidation rate, but scale adhesion was reduced, whereas at 700 °C the presence of water vapour inhibited selective oxidation of alumina and promoted internal oxidation. The authors attributed these effects to the rapid formation of transient aluminas at the lowest temperature and for all other cases, any cracking of the scale would allow ingress of water vapour which would then form weak Al–OH⁻ bonds facilitating spalling. It was proposed that the water molecule can affect the α -Al₂O₃/alloy interfacial toughness. Where the toughness was already high, low S alloys or Pt aluminide coatings for example, then the presence of water vapour had little effect. Janakiraman et al. [8] carried out cyclic oxidation tests at 1100 °C in wet and dry air on a number of alloys and coatings that form α -Al₂O₃ scales upon exposure to oxidizing conditions. The alloys that were investigated included PWA 1480, PWA 1484, CMSX 4, diffusion aluminide coatings on PWA 1480 and PWA 1484, and Co–24%Cr–10.5%Al–0.3%Y. In cases where some cracking and spalling of the alumina scales occurred in dry air, the presence of water vapour caused the degradation rate to be increased by a factor of 2. When no cracking or spalling of the alumina occurred in dry

Table 1
Nickel–base alloy compositions (wt%)

Alloy	Ni	Cr	Al	Co	Ta	W	Mo	Ti	Fe	C	Hf	Zr	Nb	Mn	Other
MarM247	Balance	8.2	5.4	9.9	3.0	9.8	0.7	1.05		0.13	1.3	0.4	0.2		B 0.01
CM186	Balance	6.6	5.7	9.2	3.2	8.5	0.5	0.7		0.07	1.4				B 0.01
Rene'N5	Balance	7.0	6.2	7.5	6.5	6.0	1.0				0.1				Re 3.0
PWA 1484	Balance	5.0	5.6	10.0	8.7	6.0	2.0				0.1				Re 3.0
PWA 1480	Balance	10.0	5.0	5.0	12.0	4.0	–	1.5	–	–	–	–	–		–
CMSX 4	Balance	6.4	5.7	9.7	6.5	6.4	0.6	1.1	–	–	0.03	–	–		Re 2.9
NiCrAl	Balance	8.0	6.0												
PM2000	Balance	20.0	5.5					0.5							Y ₂ O ₃ 0.5
Nimonic 75	Balance	19.5	0.3					0.3	2.6	0.07					
Haynes 230	Balance	26.0		5.3		4.8	1.3		3.4					0.74	
Hastelloy C	Balance	15.7		0.1			15.3	0.24	0.56	0.003				0.13	
Hastelloy X	Balance	24.0		1.45		0.19	5.3		19.0					1.03	
Inconel 718	Balance	22.0		1.0		0.90	1.9		18.0					0.38	
Inconel 625	Balance	25.0		1.03			5.7		5.4					0.55	
Nicofer 45TM	Balance	27.4							22.7	0.08				0.36	Si 2.66

Table 2
Iron–base alloy compositions (wt%)

Alloy	Fe	Ni	Cr	Al	Mn	Si	V	Mo	W	B	C	Cu	S	Nb	Ti
304L	Balance	10.2	18.5		1.4	0.6					0.03	0.3	0.01		
316L	Balance	10.6	17.2		1.2	0.3		2.1			0.15	3.1	0.002		
T91	Balance		8.7		0.4	0.26	0.23	1.0			0.10		0.001	0.09	
P92	Balance		8.72		0.47	0.16	0.21	0.45	1.87	0.002	0.09		0.06		
Kanthal AF	Balance		20.0	10.0											
10Cr– Mo– W	Balance		10.3		0.45	0.09	0.18	1.05	0.98		0.10				
HK40	Balance	19.9	24.0		0.46	1.55					0.37				
800H	Balance	31.1	20.0		0.66	0.5					0.50				
Nf616	Balance	0.06	9.0		0.46	0.04	0.20	0.47	1.84		0.10				
F17TNb	Balance		17.5			0.5					0.02			0.04	0.3

air, as was the case for low sulphur alloys, water vapour had no effect on the oxidation behaviour. It was proposed that water vapour causes stress corrosion cracking at the

Al₂O₃-alloy interface during cyclic oxidation. In tests under ambient conditions with Rene'N5 preoxidised for 1000 h at 1150 °C, Smialek and Morscher [9] also proposed that moisture at the alumina/alloy interface reduced interfacial toughness, and that this effect can be exacerbated by the presence of impurities such as sulphur segregating to the interface and thereby increasing the interfacial bond distance.

Kvernes et al. [10] studied Fe–13%Cr alloys containing up to 4.4% Al in the temperature range of 680 °C, 820 °C and 980 °C in air + 0.03–2.3% H₂O, and found that higher critical levels of Al were required for good oxidation resistance as the test temperature increased. Exclusive α -alumina formation was only detected on the alloy with 4.4% Al at 980 °C after 23 h exposure to air + 0.3% or 2.0% water vapour; at 8.5 h chromia was also found in the scale (possibly indicating removal of chromium from the scale by volatilisation). At the two lower temperatures, and for alloys with less than 4% Al, increasing the water content from 0.03% to 2.3% had a marked effect in increasing the oxidation rate by over an order or magnitude. When α -alumina was exclusively formed (at 980 °C) the oxidation rate was unaffected by the presence of water vapour.

Regina et al. [11] studied the behaviour of Fe 14% and 19% Al with 2% and 5% Cr additions at 500 °C in 2% O₂, 15% CO₂ bal N₂ with and without addition of 6% H₂O. Under these conditions γ -alumina is believed to form [12]. Only the material with a low alloy content (14%Al 2%Cr) was significantly affected by the addition of water vapour with the oxidation increasing by about a factor of seven in wet atmospheres compared with dry conditions. No explanation was proposed to account for this observation. When exposed to sulphidising environments all alloys were adversely affected by the presence of water vapour.

Zhang et al. [13] have demonstrated that a thin CVD–aluminide coating (~5 μ m thick) applied to type 304 stainless steel substantially improved the oxidation resistance in short-term cyclic tests at 700 °C and 800 °C. While no views were expressed about the mechanism of the enhanced protection it is evident that alumina scales are more resistant to attack in these environments.

Zhou et al. [14] reported that a NiCrAlY plasma sprayed coating in cyclic oxidation tests at 1050 °C in O₂ and O₂ + 5%H₂O was more severely attacked when water vapour was present. While α -alumina was formed in the dry atmosphere, a mixture of chromia, spinel and nickel oxides developed when water vapour was present. It is not clear whether alumina ever formed in the latter case, or as the authors suggested, enhanced Ni and Cr cation diffusion prevented the development of the protective layer.

Leyens et al. [15] observed that rates of oxidation of an alumina-forming MCrAlY coating were up to 25% greater in H₂/H₂O gas mixtures compared with dry air at 1080 °C and 1100 °C. They assumed that Frenkel defects are the dominant defect and attributed the increased oxidation rate to H⁺ ion substitution in the lattice creating more oxygen interstitials and vacancies.

Liu and Narita [16] demonstrated that the oxidation rate of alumina forming TiAl (CrAg) alloys containing more than 1% Ag in air at 900 °C was unaffected by the presence of 30% water vapour, with protective α -alumina-forming in both cases. The absence of Laves phase was believed to be responsible for selective oxidation of alumina.

Årterman and Hultquist [17] studied the oxidation of Fe 20%Cr 10%Al at 920 °C in various water oxygen gas mixtures. The oxidation rate in moist (about 15 mbar H₂O) air at atmospheric pressure was the same as in dry low pressure oxygen (7.5 mbar), but at

15 mbar water and either no oxygen or 7.5 mbar oxygen the rate of oxidation in relatively short-term tests (about 60 h) was approximately 2–3 times that in dry 7.5 mbar oxygen. The surface composition of the oxide formed in atmospheres containing only water vapour was richer in aluminium than when oxygen or oxygen water vapour gas mixtures were used. No interpretation of the increased oxidation rate in the presence of water vapour was provided.

In general, the conclusions of the 1996 review [3] on the effects of water vapour remain valid, that is that the kinetics of alumina formation are very little affected, but there is evidence that scale adhesion is reduced. Although it will be noted that for MCrAlY coatings, there are a few cases where water vapour significantly increased rates of oxidation, but frequently the scale failed to develop an alumina layer when water vapour was present. It appears that water vapour may have a greater effect on the initial stages of oxidation and affect the stability of the transition aluminas rather than the transport processes in the protective α -alumina layer once it is established. Tests with the different systems were conducted in water vapour with concentrations between 0.03% and 30%, but where there were observed effects, there seems to be no information about the effect of increasing the concentration of water vapour in the atmosphere in any given system.

In order to verify these conclusions, it would be of value to carry out the following experiments. Form protective α -alumina scales in dry conditions and then add water vapour to determine whether or not the reaction rate or scale adhesion was altered by the introduction of water vapour.

2.2. Chromia

There is a great deal information about the effects of water vapour on chromia-forming materials and depending on the system different behaviours are observed. This section, therefore, will consider separately the kinetics of chromia formation on chromium metal, iron-base ferritic and austenitic alloys and nickel-base alloys.

2.2.1. Chromium metal

The growth rate of chromia formed on pure chromium metal seems to be only slightly increased by the presence of water vapour [18–21]. Jacob et al. [18] found that the oxidation rate at 800 °C and 1000 °C was about 15% higher when 1% (1000 Pa) water vapour was added to argon/oxygen mixtures, but that the rate was reduced by about 60% when 1% water vapour was present in nitrogen/oxygen mixtures. They proposed that when nitrogen was the carrier gas competitive adsorption reduced the effect of water vapour. For the Ar/O₂ experiments the oxidant was found to be largely derived from water vapour even though only present in small amounts, but this had little effect of the oxidation rates, so it is clear that the transport processes were not greatly affected. However for the N₂/O₂ gas mixtures, scale cracking was evident in the absence of water vapour, it seems that the scale was more plastic when water vapour was added, and in part this might be explained by the smaller oxide grain size for the scale grown in the presence of water vapour compared with that grown under dry conditions. Hulquist et al. reported [19] that at 900 °C rates were approximately doubled in 2% water vapour (20 mbar) and in a 1% oxygen/1% water vapour mixture (10 mbar/10 mbar) compared with the rate in dry oxygen at the same total pressure. The adhesion of the scale was also improved when the scale

was formed in water vapour containing atmospheres, and this was attributed to a greater fraction of the scale growing at the metal/oxide interface. It was also demonstrated that a higher hydrogen content of the metal also led to slightly increased rates when water vapour was present. At higher levels of water vapour (Ar 15% H₂O), Henry et al. [20] observed that the oxidation rate at 900 °C was higher than in an Ar 15% oxygen gas mixture. They proposed the increased rate of growth was due to the smaller ionic radius of the OH[−] (95 pm) compared with O^{2−} (140 pm), and also, in agreement with the work of Hultquist et al. [19], scale adhesion was also significantly improved when water vapour was present compared to the case for dry oxygen. Hansel et al. [21] showed that for Cr oxidised at 1000 °C at high pO₂ values there was no effect of up to 8% water vapour, but when water vapour was present in reducing environments (Ar · 4% H₂ gas mixtures) rates were increased by about 50% compared with rates of oxidation in Ar · 4% O₂ and the formation of blades was observed. They proposed a model, in which oxide growth was sustained by diffusion of chromium vacancies and adsorption of H₂O on oxide exposed to low oxygen-activity gas led to the formation of hydroxyl species. At high oxygen activities, molecular oxygen adsorbs preferentially on the entire surface, overwhelming any local variation due to catalysis of H₂O dissociation. This explained the absence of whiskers in high oxygen content atmospheres.

In the results presented above, the effect of evaporation of the volatile CrO₂(OH)₂ compound do not seem to be significant in terms of altering the rate of oxidation, probably due to the fact that supply of chromium from the substrate is not rate limiting.

2.2.2. Chromia-forming alloys

Douglass et al. [3] in their 1994 review stated that water vapour has a major effect on the oxidation rate of chromia-forming alloys and that this was most marked for the iron-based alloys. There was a plea for comparative studies and new information about the behaviour of Ni Cr and Co Cr based systems, but it seems that very little new information has been published. In general, for the iron chromium-containing alloys it is found that oxidation rates were increased by the addition of water vapour to the atmosphere compared with oxidation under dry conditions [2,22–36] (see Fig. 2 for example). Rates generally increased by more than an order of magnitude after an initial period of protection was observed; this breakaway oxidation was a consequence of failure of the protective chromia layer with subsequent rates being controlled by the base alloy. In many cases failure of the chromia layer was attributable to formation of the volatile hydroxides CrO₂(OH)₂ and Cr(OH)₃ [22,30,37–43] although it should be noted that this explanation is only valid at relatively high oxygen partial pressures (see later discussion of oxide volatility). Very recently, however for 9% Cr steels, Ehlers et al. [36] suggest that volatile Fe(OH)₂ forms at low p(O₂) in the inner layers of the scale and is then converted to haematite or magnetite in the outer layers of the scale so contributing to the higher rates of oxidation observed. Galerie et al. [23] show that the first stage of breakaway of Fe 15%Cr at 800–1000 °C in Ar 15% H₂O corresponds to separation of the chromia scale from the alloy and consequent scale equilibration allowing the formation of haematite at the metal/oxide interface. Then rapid growth of haematite at this interface disrupts the chromia scale and breakaway ensues. They propose that the more acidic nature of haematite compared to chromia encourages more rapid dissociation of water and thus continued haematite growth is favoured, whereas in the absence of water vapour chromia would continue to form and protection maintained. Fujii and Meussner [24] oxidised a range of Fe,

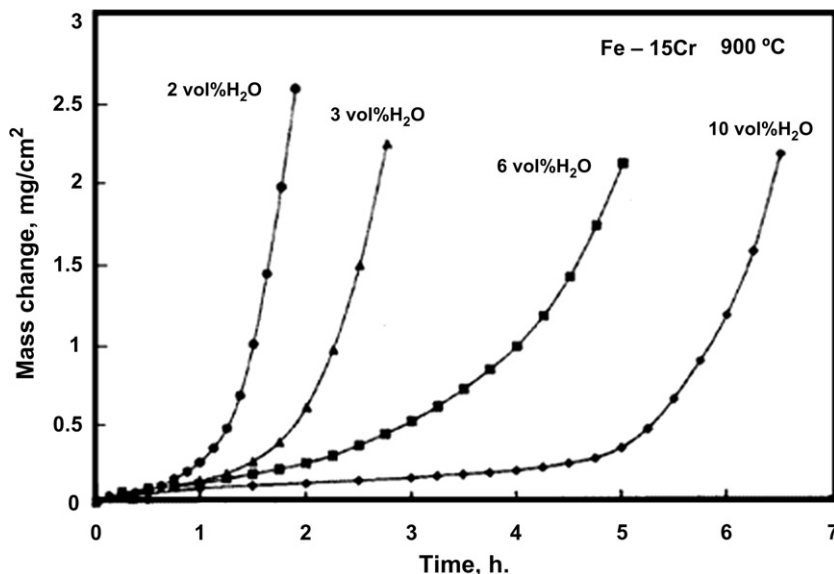


Fig. 2. Oxidation kinetics of Fe-15Cr in oxygen containing different amounts of water vapour at 900 °C, after Ref. [31].

Cr with up to 25%Cr alloys at up to 700–1100 °C in Ar 10% water vapour and contrary to most other work observed a period of protective oxidation for the alloys with Cr contents greater than 20%Cr. They proposed that the high rates of oxidation were related to hydrogen/water dissociation in pores within the wüstite layer (see later discussion of iron oxides). Mikkelsen and Linderot [26] explained the breakaway oxidation of Fe 22%Cr at 800 °C in a H₂/Ar gas mixture (7:93) with addition of 12% water vapour as a consequence of the stability of fast growing wüstite, with 1% water vapour wüstite is not stable. Cheng et al. [27] propose that the nickel particles found in the thick scale formed on 316L stainless steel during breakaway oxidation in an air 10% water vapour gas mixture at 1030 °C catalysed the decomposition of water and thus led to the observed increase in oxidation rate. Yang et al. [28] and Nakagawa et al. [29] considered the case where different oxidation processes were occurring on two sides of Fe–Cr alloys when used, respectively, as interconnect material in the solid oxide fuel cell (SOFC), or as a boiler tube material for power stations. It was proposed that hydrogen generated on one side of the alloy diffuses to the side with a higher p_{O_2} and in doing so changes the transport processes of the protective chromia to promote more rapid diffusion of iron and thus accelerate attack. Peng et al. [30] and attributed breakaway oxidation of 304L stainless steel at temperatures up to 900 °C in air water vapour mixtures (2–40% H₂O) to loss of chromium by formation of $\text{CrO}_2(\text{OH})_2$, but interestingly by applying a coating of the same material with a columnar grain structure with a diameter of about 12 nm no breakaway was observed after 25 h at 900 °C. The rapid supply of chromium by grain boundary diffusion was believed to be responsible for the improved behaviour, although eventually this would become depleted and thicker coatings would therefore be required. Long-term stability of the nano-structured coating is claimed due to pinning the columnar grains to the substrate alloy. It is worth noting that the scale that formed on the nano-structured coating had an outer layer

composed of MnCr_2O_4 which is claimed by Holcomb and Alman [44] to reduce volatilisation by factors of up to 55. Jianian et al. [31] propose that the failure of a protective chromia scale on Fe 15%Cr and Fe 20%Cr alloys at 900–1000 °C in air and up to 20% water vapour is the result of through scale cracking which then admits water vapour to the alloy/scale interface where it reacts with the alloy forming Fe_2O_3 and H_2 , the hydrogen then reduces the chromia, and chromite is then formed by reaction with haematite ($\text{Fe}_2\text{O}_3 + 4\text{Cr} + 5\text{H}_2\text{O} = 2\text{FeCr}_2\text{O}_4 + 5\text{H}_2$). Volatilisation was disregarded as a possible mechanism since the presence of a surface layer of ceria was sufficient to prevent breakaway from occurring in these air/water vapour gas mixtures. In many cases cited above, hydrogen diffusion into the metal was observed, a clear sign of direct reaction of the water vapour in the oxidation process.

The effect of water vapour concentration on kinetics has been studied by a number of groups [25,27,31,26,24,32,33]. In general, with increasing amounts of water vapour in the atmosphere the time to the onset of breakaway oxidation was reduced but that the rate of oxidation in the breakaway phase was approximately independent of the water vapour content of the atmosphere (see, for example, Fig. 2). When very small amounts of water vapour were present (for example, 0.09%) [32] or when only short-term tests were carried out [33] then the oxidation rate was dependent upon the water content of the atmosphere.

For the nickel-base system some early work by Rahmel [45] showed that Nimonic 75 was unaffected by the presence of 50% and 100% water vapour in short-term tests (25 h) at 1100 °C compared with the behaviour in an O_2 50% CO_2 gas mixture. Similarly Wood et al. [46] observed no difference between oxidation in Ar 10% water vapour and oxygen. England and Virkar [47,48] studied the oxidation of a series of thin foil nickel-based alloys (Inconel 625, Inconel 718, Hastelloy X and Haynes 230) in air and wet hydrogen ($p(\text{O}_2)$ 10^{-21} – 10^{-16} atm, $p(\text{H}_2\text{O})$ 0.07 atm at 700–1100 °C). At 800 °C the oxidation rate was increased in wet hydrogen by factors ranging between 8 and 30, but at 1100 °C the effect of wet hydrogen was to decrease the oxidation rate compared with air by factors ranging between 1.5 and 13. The activation energies for wet hydrogen oxidation were approximately half those for air (~ 340 kJ mol $^{-1}$ compared with ~ 180 kJ mol $^{-1}$). Hussain et al. [49,50] reported that Hastelloy C-4 formed a protective scale in 100% steam at all temperatures in the range 600–1200 °C whereas the scale spalled when formed in air. Surprisingly there was no evidence for the volatilization of chromia as $\text{CrO}_2(\text{OH})_2$ when a Ni 25%Cr 0.01%Y alloy when oxidised air +5% H_2O at 950 °C for exposures of up to 4000 h [44]. The same alloy with additions up to 3%Mn spalled so that any volatilisation was masked. Calculation showed, however, that if an external layer of MnCr_2O_4 formed, rates of volatilisation could be reduced by factors of up to 55 [44]. The same calculations would apply to the Fe–Cr system.

The limited information on NiCr alloys is somewhat surprising, especially in view of the widespread use of such materials in corrosive combustion systems, waste incineration for example, and for anticipated application for ultra supercritical boilers now being developed for power plant. The very surprising observation that volatilization of chromia as $\text{CrO}_2(\text{OH})_2$ does not seem to occur should be verified. The work of Hussain and co-workers [49,50] suggests that Ni-containing oxides may be unaffected by the presence of water vapour. However, from the work of Zhou et al. [14] where it was shown that in the presence of 5% water vapour in oxygen resulted in an increase in the oxidation rate of an alumina-forming NiCrAlY coating compared with the rate in dry oxygen at 1050 °C. When moisture was present the scale consisted of NiCr_2O_4 , NiO and Cr_2O_3 and high mass gains

were observed (3 mg cm^{-2} after 400 h) suggesting that Ni Cr alloys are susceptible to attack by water vapour.

It would seem that the reported difference in the behaviour of pure chromium metal and chromia-forming alloys is that for the former, transport processes within the scale are altered by water vapour causing relatively small changes in the oxidation rate, whereas for the latter the presence of water vapour may reduce the ability of the alloy to form a protective scale, so that the oxidation rate is then controlled by that of the base alloy, and thus very large increases in oxidation can be observed. The mechanisms proposed by the different researchers will be discussed in more detail when considering transport processes, but the major difference between Fe-base and Ni-base alloys suggests that the inability to form chromia as a result of scale cracking or volatilisation is compounded in the case of the Fe-base system by a further water vapour induced acceleration of oxidation for the iron oxides which does not occur for the nickel system.

2.3. Silica

The fundamental work of Deal and Groves [51] on the oxidation of silicon is widely acknowledged to provide a solid basis for understanding the formation of silica in dry and wet atmospheres. They derived the following relationship: $x_0^2 + Ax_0 = B(t + r)$, where x_0 is the oxide thickness, B is parabolic rate constant, B/A is the linear rate constant and r is the initial oxide thickness. At small thicknesses the rate is approximately linear and at high thickness it is parabolic. The linear rate results from the interfacial reaction, Si–Si bond breaking, and the parabolic rate is due to diffusion controlled processes. Both parabolic and linear rate constants are more than an order of magnitude greater in wet than dry oxygen in range 920–1200 °C [51] (see Fig. 3). The main diffusing species in dry conditions is molecular oxygen (note this is the superoxide ion O_2^-), whereas in wet conditions it is molecular water. In wet gas the constant rate is proportional to the equilibrium concentration of molecular water which is three orders of magnitude greater than oxygen. Irene [52] proposed that the initial model can be improved by consideration of the presence of micropores, while Bhat et al. [53] have shown that for very thin oxides the oxidation rate at 800 °C increases with increasing water vapour content (Fig. 4).

Deviations from Deal–Grove are found for the first tens of atomic layers of oxide which are critical for the ultra-thin oxide layers now demanded. Several features are deemed to be important; firstly the rôle of stress generation and relaxation. Secondly the nature of the oxide closest to the Si substrate is believed to be different both in defects and structure from the amorphous stoichiometric oxide further out. Finally, the charge states of both fixed and mobile species are not the same as in thicker oxides films [54]. Several models have been developed for this region of oxide growth [55,56] but a description is beyond the scope of this review.

The use of SiC and Si_3N_4 for high temperature applications in combustion environments has stimulated a body of research on the effects of water vapour at temperatures in excess of 1000 °C. Under these conditions the reaction of silica with water vapour to form the volatile hydroxide $\text{Si}(\text{OH})_4$ plays an important rôle in acceleration of the oxidation process [57–59]. Typically, for SiC, oxidation rates were about an order of magnitude higher in $\text{O}_2/90\% \text{ H}_2\text{O}$ at 1400 °C than those found under dry conditions, and the rate constant shows a power law dependence on $p(\text{H}_2\text{O})$ between 0.5 and 1 (Fig. 5). For growth controlled by diffusion of molecular water, $n = 1$, and for growth controlled by OH^-

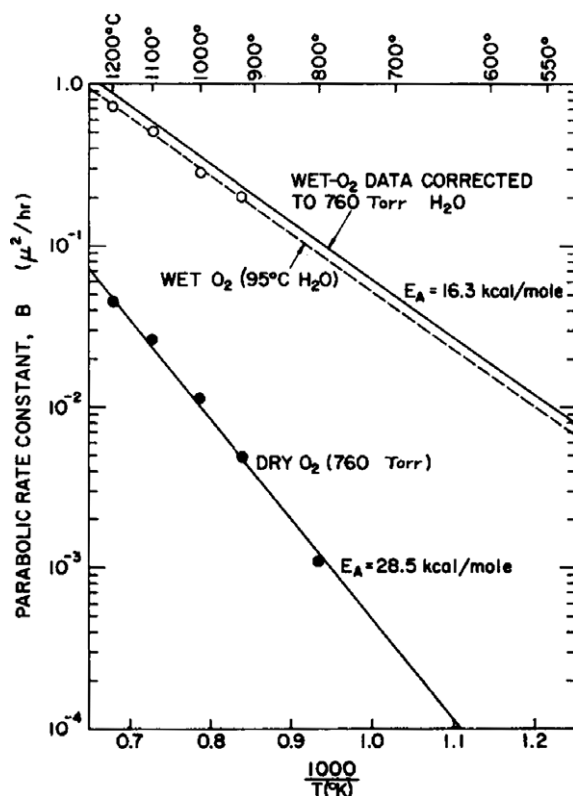


Fig. 3. The effect of temperature on the parabolic oxidation rate of silicon, after Ref. [51].

diffusion, $n = 0.5$. Opila [57] therefore concludes that both species are involved in the growth of amorphous and crystalline silica at 1200 °C and 1400 °C, respectively. At lower temperatures (600 °C and 700 °C) for MoSi_2 in oxygen 10% water vapour mixtures, the presence of Mo was found to be beneficial in establishing a protective layer of silica. Differences in the volatility of $(\text{MoO}_2(\text{OH})_2)$ and $(\text{MoO}_3)_3$ allowed the establishment of a compact protective silica layer sooner in the water vapour containing atmosphere than on dry oxygen [60].

The formation of an amorphous silica inner layer was effective in reducing the oxidation rate of an Fe 9%Cr alloy to about half that of an essentially Si-free steel (0.06%Si) at 700 °C in steam when alloyed with 0.5% Si, but the effect of silicon is less beneficial at lower temperatures (500 °C) [61]. Similar beneficial effects of silicon additions of up to 1% to Fe · 15%Cr were reported by Wouters et al. [62]; Fig. 6 is an electron micrograph showing the presence of a well developed layer of silica at the alloy/oxide interface. However the authors doubt whether the silica layer inhibits iron transport through the scale since the silica does not possess the same insulating properties that were observed when it was formed under dry conditions.

Ueda et al. [63,64] showed that the eventual formation of a silica layer on a 9Cr steel (T91) containing 0.25% Si during oxidation at 700 °C in an Ar 15% H_2O gas mixture led to the disappearance of the initially formed internal oxidation zone (IOZ) and at the same

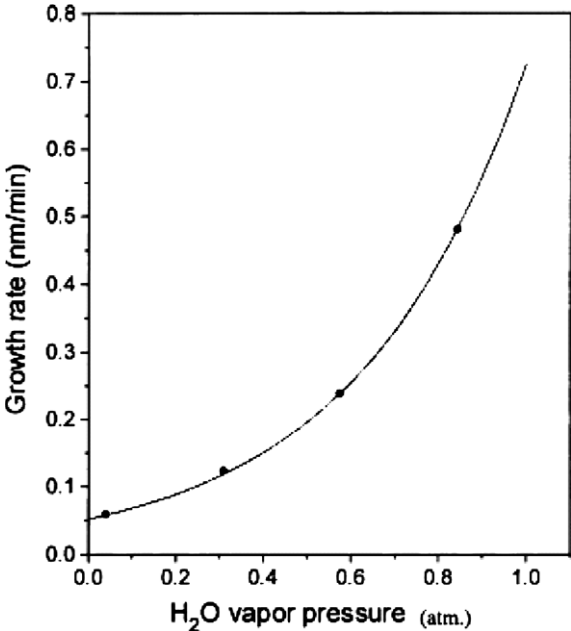


Fig. 4. Oxidation rate of silicon at 800 °C as a function of water vapour pressure, after Ref. [53].

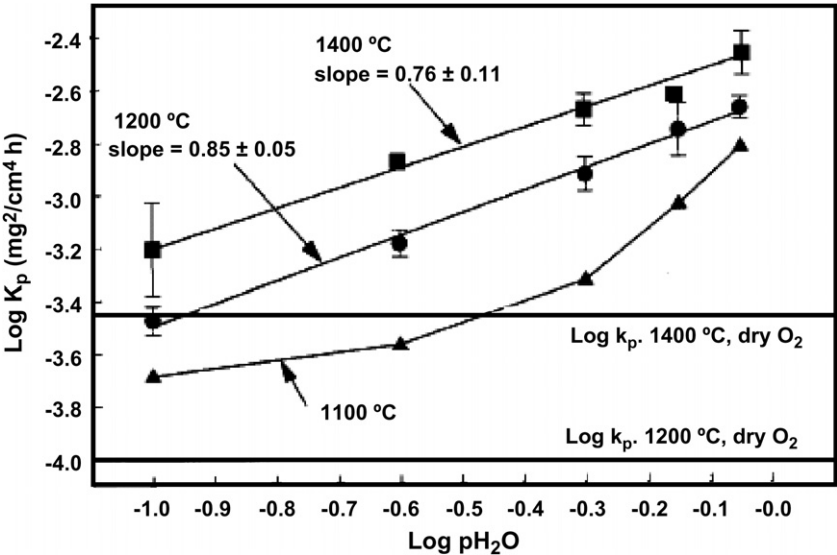


Fig. 5. Parabolic rate constant for SiC as function of p(H₂O), after Ref. [57].

raised the p(O₂) at the silica/internal oxide interface such that FeO could be formed and thus eliminate the internal oxide zone. The oxidation kinetics were linear during the IOZ stage but became protective once the silica layer was established after about 28 h. The

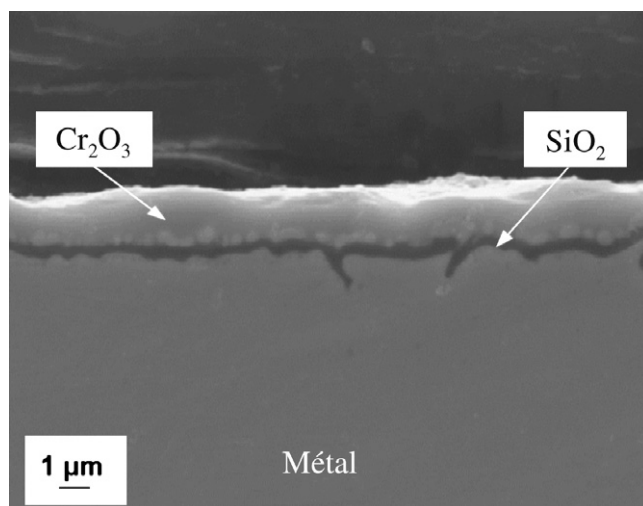


Fig. 6. Scanning electron micrograph of a cross-section of Fe 15%Cr - 0.5%Si, oxidised at 950 °C in Ar 150 mbar H₂O for 8 h, after Ref. [62].

linear kinetics indicate a surface controlled reaction leading to a high $p(\text{O}_2)$ initially at the scale IOZ interface. Eventually the scale becomes sufficiently thick such that mass transport in the scale becomes rate controlling causing a drop in the $p(\text{O}_2)$ at the scale IOZ interface to allow formation of a silica layer. Ishitsuda et al. [61] carried out a detailed study of the effect of Si additions between 0.06% and 0.49% on the 9Cr steel in the temperature range 500 °C – 700 °C in high pressure (35 MPa) steam, and concluded that silicon was most effective in reducing the oxidation rate at the highest temperature tested and at the highest silicon content, where rates were reduced to 50% of that observed with the low Si alloy. As with the work of Ueda et al. [63,64] the establishment of a complete silica layer was responsible for the protective behaviour at the highest test temperature.

2.4. Titania

Wouters et al. [65] reviewed the well established effect of water vapour in increasing the oxidation rate of titanium compared with that observed under dry conditions. For example at 850 °C mass gain was increased by about a factor of three in 20 mbar H₂O compared with the rate in 20 mbar O₂. In the temperature range 650–850 °C, the rate of oxidation was directly proportional to the water vapour content and parabolic kinetics were observed. Hydrogen was found in the metal after exposure and there was no change in the conductivity of the oxide which remained n-type. Wouters et al. propose that the increased rate of oxidation result from incorporation of OH[−] in the lattice and the more rapid diffusion associated with the smaller ionic radius than the oxide ion.

Another system of interest in which titania scales can form is the intermetallic titanium aluminide, although in this case for optimum protection alloys are usually designed to form alumina by additions of Cr and Ag. There are a number of reports in the literature [66–68] that the oxidation rate of titanium aluminides is increased in moist atmospheres compared with dry conditions for alloys where alumina does not form. Zeller et al. [66]

observed that the rate of oxidation of Ti 47% Al 1% Cr 1% Si doubled at 700 °C when 10% H₂O was present in the air compared with the rate under dry conditions. Exclusive formation of alumina did not occur for this alloy under either set of conditions, but instead a mixed alumina titania scale formed. The effect of water vapour was to alter the morphology and microstructure of the titania. Upon changing conditions from wet to dry air there was an immediate decrease in oxidation rate. The authors attributed the effects to changes in defect chemistry of the rutile which resulted on preferential crystal growth and altered morphology of the rutile phase. Taniguchi et al. [67] studied the oxidation of Ti 36.5% Al at 1100 and 1200 K (827 and 927 °C) in oxygen and oxygen water mixtures. While the oxidation rate increased only relatively slowly with increasing water contents of the gas at 1100 K, only a 5% addition at 1200 K resulted in more than two orders of magnitude increase in rate compared with dry conditions. Under these latter conditions a two layered porous scale was formed consisting of an outer more porous rutile layer and an inner less porous mixture of alumina and rutile. It was proposed that hydrogen dissolving in the rutile changed the defect structure and thus accelerated oxidation. In agreement with the work of Zeller et al. the titania crystal morphology was also changed due to the presence of water vapour. Brady et al. [68] studied a series of Ti Al Cr alloys at 1000 °C in dry and moist air. For those alloys which do not contain a Laves phase, Ti(CrAl)₂, oxidation rates in moist air were increased by over an order of magnitude compared with dry conditions. In this case the authors proposed that the effect of water vapour was directly related to the composition of the phase(s) present at the metal/scale interface and thus the ability to form a protective alumina scale.

2.5. Iron oxides

Rahmel and Tobolski [69] studied the oxidation of iron in the temperature range 750–950 °C in oxygen/water vapour mixtures with 2–69% water vapour. They reported that at 750 °C there was no effect of water vapour on the oxidation rate, but that at 950 °C and with the highest concentration of water vapour the rate was increased by a factor of 1.6. The scale had an outer compact layer and an inner porous layer and hydrogen also dissolved in the metal. It was proposed that increased oxidation in the presence of water vapour was due to a dissociation reaction in the pores of the oxide which contained H₂O and H₂. Reduction of the oxide occurs at the outer edge of the pore and oxidation of iron ions or metal at the inner surface, thereby transporting oxygen inwards to accelerate the reaction. For this mechanism to operate it is necessary for either hydrogen or water to penetrate the scale and enter the pore. The initial suggestion made by Rahmel and Tobolski was that water penetrated the scale due the formation of micro-channels according to a mechanism first proposed by Mrowec [70] in which it is suggested that the faster diffusion of cations in the grain boundary compared with lattice will cause the grain boundary region to open up. However, as pointed out by Kofstad [71] it would be expected that gas access down the open channel would allow oxidation to occur there and thus close the grain boundary channel. He proposed that the presence of channels is the result of creep and plastic deformation of the scale. It is proposed that either protons dissolve in the outer scale and diffuse inward to interact with the pore or water is transported through micro-cracks in the scale.

Tuck et al. [72] found similar results for pure iron in 12% water vapour plus oxygen at 950 °C where the rate was increased by about a factor of two relative to that found in

oxygen alone when the specimens were heated in Ar prior to the introduction of the reactant gas, but they noted that iron oxidized at the same rate in pure steam as is in oxygen at 950 °C when heated to the test temperature in an oxidising environment. Mild steel generally oxidized more slowly than pure iron in oxygen, but when water vapour was added the rates of oxide growth were the same. The oxidation rate of the mild steel was increased in the presence of steam whether heated in Ar or the oxidising atmosphere. Both compact and porous inner layer scales were formed in the oxygen 12% water vapour mixture, whereas in oxygen spallation occurred. The compact layers were only found on flat specimens of pure iron whereas porous scales were formed on all specimen shapes of mild steel. Evidently plasticity had been increased by the presence of steam. It was proposed that hydrogen dissolved in the scale and enhanced plasticity by providing additional sources and sinks for dislocation movement and by increasing the volume of the distorted zone around the dislocation thus permitting easier movement. When pores were present the Rahmel Tobolski [69] mechanism operated, whereas for the compact inner layer scale enhanced lattice diffusion in wüstite was proposed.

2.6. Scales formed on dilute iron alloys

Hayashi and Narita summarised [73] the behaviour of dilute iron-base alloys as follows. It is widely accepted that the oxidation of dilute iron alloys containing aluminium, chromium or silicon in water vapour containing atmospheres is represented by S-shaped curves, which consist of three oxidation stages, the first slow, the second rapid, and the third slow oxidation. The first slow oxidation produced a thin outer Fe_3O_4 and Fe_2O_3 layer, over a thin, protective intermediate layer, consisting of Cr_2O_3 , SiO_2 , or Al_2O_3 as well as their complex oxides containing iron. The duration of the first slow stage varies, depending on gas composition, temperature, and alloying elements. During the second rapid oxidation, a thick duplex-structure scale formed with an outer Fe_2O_3 , Fe_3O_4 , and FeO layer and an inner layer containing FeO and complex oxides containing Fe and alloying elements. The inner layer is porous, containing a number of small voids. Relatively large voids are found in the outer layer and these tend to array along the oxide grain boundaries, as demonstrated by Rahmel and Tobolski [69] and Fukumoto et al. [74]. The third stage of corrosion is characterized by slow oxidation, but the scale structure has not been fully established.

Narita and co-workers have carried out extensive studies of the effects of water vapour on dilute iron alloys with 5% aluminium [73,75] at 800 °C and silicon [74] at 800 °C and 1000 °C with a range of gas mixtures containing Ar, N_2 , O_2 and H_2O . For Fe 5%Al in N_2 – O_2 – H_2O mixtures the rate of oxidation was inversely proportional to the oxygen content; O_2 12.2% H_2O having the lowest rate and N_2 –0.9% O_2 12.2%– H_2O the highest rate, but with N_2 – O_2 – H_2O mixtures with less than 0.9% O_2 the rate decreased. The rate of oxidation was dependent on the $p(\text{H}_2\text{O})/p(\text{O}_2)$ ratio, and a maximum was observed at a ratio of between 5 and 10 [73]. Changing the oxidising atmosphere from O_2 12.2% H_2O or N_2 12.2% H_2O to N_2 0.9% O_2 12.2% H_2O after 4 h oxidation resulted in an immediate increase in the oxidation rate for the case of the N_2 12.2% H_2O gas mixture but the rate only increased after 30 min for the O_2 12.2% H_2O gas mixture. Reversing the procedure in which tests were started in the more aggressive N_2 0.9% O_2 12.2% H_2O atmosphere and then changing to the O_2 12.2% H_2O or N_2 12.2% H_2O resulted in an initial increase in rate before the rate decreased to that found in the respective atmospheres [75]. It was proposed

that in the gas mixtures containing increased levels of oxygen a more complete layer of Fe_2O_3 formed and this reduced the oxidation rate.

With the Fe 1.5% Si alloy, water vapour again accelerated the oxidation rate, and inward movement of oxidant was encouraged by water vapour. In tests with 10.5% H_2O added to O_2 , air and Ar, high rates were observed from the outset with the Ar gas mixture, but with air and O_2 gas mixtures incubation periods were observed before break-away occurred; the longer incubation period was for the tests in the oxygen-rich gas mixture [74].

2.7. Nickel oxide

As with NiCr alloys there is very little information on the behaviour of pure Ni. Here the work of Rahmel [45] clearly shows that water vapour has little effect on the oxidation of pure Ni at 1000 °C and 1100 °C in short-term tests of up to 7 h, with k_p values of $2.8 \times 10^{-8} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and $1.3 \times 10^{-7} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$, respectively, for O_2 43% Ar and O_2 43% H_2O gas mixtures. When nickel was annealed in vacuum to reduce the H_2 content from about $0.5 \text{ cm}^3/100 \text{ g H}_2$ to $0.009 \text{ cm}^3/100 \text{ g H}_2$, a slight increase in the oxidation rate in O_2 10% H_2O at 1080 °C was observed compared with the rate in pure oxygen (k_p values; $1.1 \times 10^{-7} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ compared with $0.85 \times 10^{-7} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$). The results were explained on the basis of a higher decomposition pressure of NiO compared, for example, with iron oxides so that “oxygen bridges” were maintained between the oxide and metal and thus preventing pore development and direct access between water vapour and the nickel.

3. Scale morphology

The effect of water vapour on oxide microstructure can be seen in whisker formation, changes in pore formation and in oxide grain size. These three aspects will be considered separately in the following section.

3.1. Whisker formation

In the Section 2 on kinetics, whiskers were frequently reported when water vapour was present in the environment [21,32–34]. The mechanism for whisker formation discussed by Raynaud and Rapp [76] and first proposed by Tallman and Gulbransen [77] that is generally accepted involves surface diffusion inside a hollow structure that results from the presence of a dislocation in the oxide. Growth of the whiskers is more pronounced in water vapour containing atmospheres because of faster dissociation of water vapour compared with oxygen, for example. Zeng and Young [34] also observed whisker formation in CO_2 containing gas mixtures, and suggested that a similar mechanism operated with easy dissociation of the CO_2 molecule. They also suggest that an important aspect of whisker formation is that the tip of the whisker is catalytically active in promoting dissociation of the oxidant. It is evident that the growth of whiskers is controlled by a surface reaction and thus linear kinetics will be observed, but as the oxide thickens then the rate limiting process for scale growth is then diffusion controlled. The dissociation of oxidant species will be discussed in more detail in Section 5.1.

Raynaud and Rapp [76] also point out that whiskers formed on nickel oxide when nickel was exposed at 1000 °C to moist oxygen in an environment scanning electron

microscope at a pressure of 3×10^{-4} atm. It will be recalled that in Section 2.7 the effects of water vapour on the kinetics of oxidation of nickel were negligible, although, as just reported, the details of oxide morphology may be modified by the presence of water vapour without significantly altering the kinetics of oxidation.

3.2. Scale porosity

Porous scales are frequently observed when water vapour is present, particularly if there are large changes in the kinetics of oxidation. The oxidation of pure iron and of iron chromium alloys are good examples of this type of behaviour. In the case of iron, it will be recalled that the observation of porosity was related to the geometry of the specimen for high purity material, where Tuck et al. [72] observed compact scales on flat surfaces but porous scales on curved surfaces. For mild steel no such distinction was observed. Thus, it would appear, that for iron at least, the formation of pores in the scale is not a direct consequence of water vapour itself, but rather the result of the high rates of oxidation that are caused by the presence of water vapour. However, for the case of iron and its alloys, the fact that a porous structure exists gives rise to the Rahmel–Tobolski [69] mechanism for enhanced oxidation in which the oxidant is transported across the pore by a dissociation reaction. New oxide is formed at the metal/oxide side and oxide dissociates at the oxide/gas side so that the pore moves outward through the scale. As discussed previously, water vapour is required to penetrate the scale for this mechanism to operate, and it is believed that this occurs via micro-cracks or by transport of protons. The pores generally form at the metal/scale interface due to vacancy condensation for scales growing by cation transport. The enhanced scale plasticity reported by Rahmel and Tobolski [69] and Tuck et al. [72] allows contact to be maintained with the substrate and thus oxide growth is maintained, whereas in the absence of water vapour porosity does not develop but the scale loses contact with the substrate.

Voids and channels at oxide scale grain boundaries formed on dilute Fe–Si and Fe–Al alloys in water-containing atmospheres were reported by Narita and co-workers [73–75] and they proposed that these formed by the Mrowec “perforating” mechanism, although this has been discounted by Kofstad [71] who prefers plasticity or creep induced deformation as an explanation of the voids and grain boundary channels. It will be recalled that both Rahmel and Tobolski [69] and Tuck et al. [72] reported enhanced plasticity of iron oxide scales, thus supporting the creep/plasticity induced mechanism for pore and micro-channel formation.

A system that has been extensively studied in the literature is iron chromium alloys with 9–12% Cr that are used in many boilers. In this case, in the absence of water vapour a protective chromium-rich spinel scale develops, but upon introduction of water vapour breakaway oxidation occurs. Quadakkers et al. [78] have suggested a scheme for the development of the thick breakaway scale as shown in Fig. 7. The breakdown of the protective spinel scale is accompanied by formation of a rapidly growing magnetite layer and an inner scale consisting of Cr_2O_3 precipitates in an “FeO-matrix”. The inner and outer layers are separated by a gap, perhaps caused by vacancy condensation resulting from the rapid growth rate of the outer magnetite layer. Further growth of the scale depends to a large extent on transport processes within this gap, where the so-called “ $\text{H}_2/\text{H}_2\text{O}$ -bridges” proposed by Rahmel and Tobolski [69] provide the transport mechanism. Additionally, molecular gas transport occurs through the outer scale [79]. As the overall scale

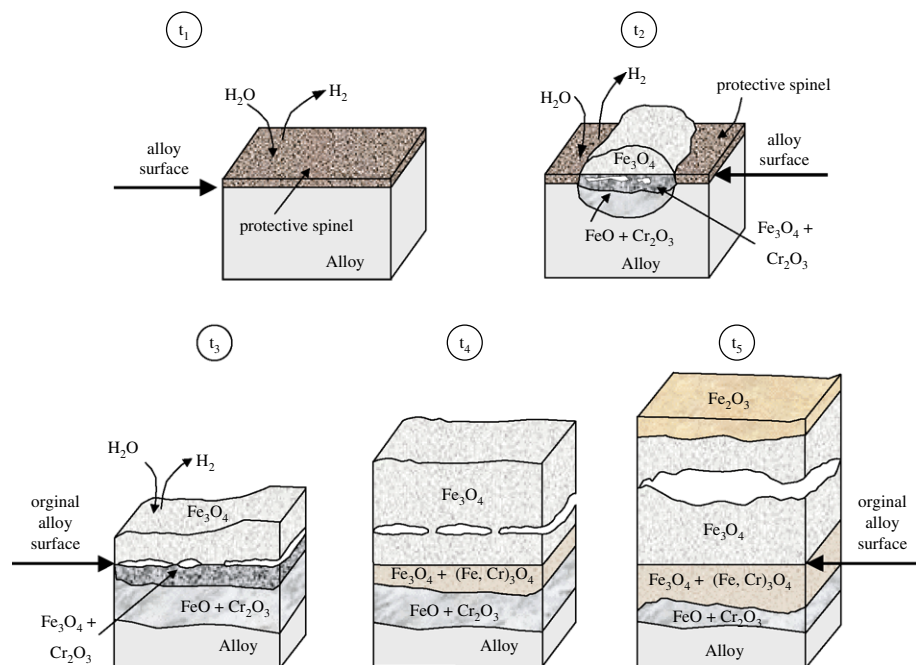


Fig. 7. Schematic illustration showing scale formation of 9–12%Cr steels in Ar–H₂O mixtures in the temperature range 550–650 °C. Exact mechanisms and times depend on steel composition and exposure temperature. In case of 10Cr–Mo–W steel at 650 °C the time t_5 is approximately 2–5 h, after Ref. [78].

thickness increases, the Fe-activity at the scale/gas interface gradually decreases due to the increasingly difficult transport of Fe cations to the oxide surface as a result of the presence of the large gap that develops (Fig. 7). This decrease in iron-activity gradually results in formation of haematite, i.e. the oxide in equilibrium with the gas atmosphere, on top of the scale. The further development of the scale now depends very much on the temperature. Upon prolonged exposure, the scales start to develop more and more micro-voidage that develops first in the inner scale. Quadakkers et al. [78] noted that the pore distribution was very dependent upon alloy purity and temperature, and they propose that this depends on the way in which the vacancies within the scale and/or the scale/alloy interface coalesce to form pores. The latter seem to be affected by the presence of “condensation-sites” such as carbide precipitates. Fig. 8 shows examples of scale morphology that develops on 9% Cr steels after prolonged exposures.

Porosity is also observed within chromia scales that were formed in water vapour containing atmospheres, whereas under dry conditions porosity was confined to the metal/scale interface [20]. As will be discussed later, the effect of water vapour on transport mechanisms within chromia scales is to increase cation vacancies and thus chromium diffusion is enhanced leading to vacancy condensation and pore formation. At the same time, however, there is an increase in inward diffusion of oxidant due to the effective diffusion of OH[−], and Henry et al. suggest [20] that the pores become incorporated in the growing scale. Fig. 9 compares the morphology of chromia scales grown in dry and moist conditions where the differences in pore formation are apparent.

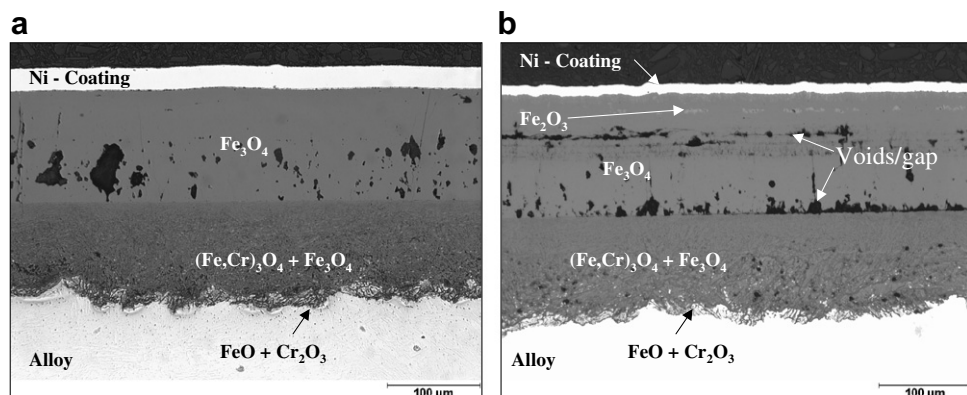


Fig. 8. Typical examples of different types of void/gap formation in outer magnetite on 10Cr–Mo–W steel during long-term exposure in Ar–50% H_2O . (a) 3000 h, 650 °C; random orientation of voids, (b) 10,000 h, 625 °C; void concentration at interface between inner and outer layer, after Ref. [78].

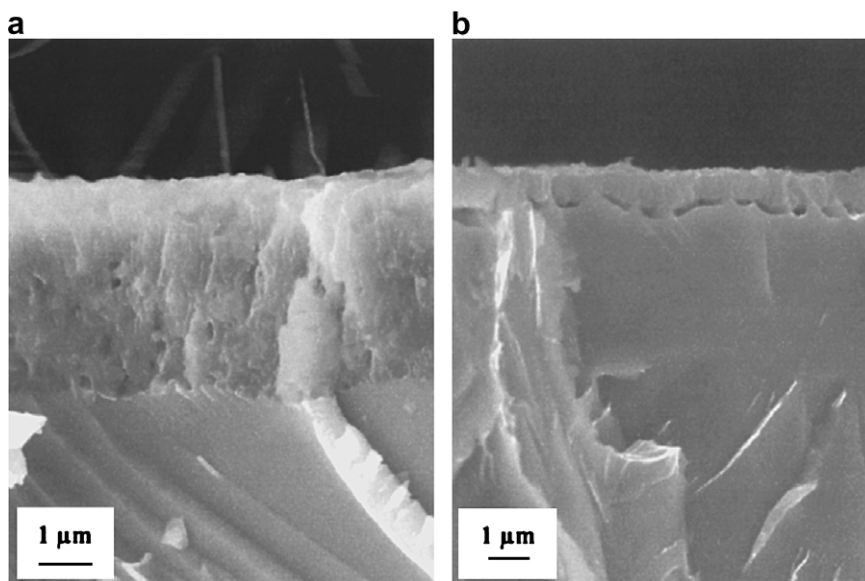


Fig. 9. Scanning electron micrographs of scales formed on chromium specimens oxidized at 900 °C: (a) in 150 mbar H_2O for 5 h; (b) in 150 mbar O_2 for 1 h (oxide on top, metal at the bottom) after Ref. [20].

Ehlers et al. [36] have demonstrated when the haematite magnetite system formed on 9% Cr steels is grown in moist oxygen it is gas permeable, but if formed in dry oxygen it is not. If the moist gas is exchanged for a dry gas during the oxidation, the scale remains permeable indicating that water vapour is preferentially adsorbed on the internal surfaces preventing further reaction and closure by reaction with oxygen. This is in contrast to result reported by Pieraggi et al. [32] who demonstrated that the outer scale formed on a low Cr steel in dry air (H11) was gas permeable. These apparently contradictory results

may be explained by the different conditions under which the scales were formed. The work reported by Pieraggi et al. was carried out at a low $p(\text{O}_2)$ in an environmental scanning electron microscope while that by Ehlers et al. was at atmospheric pressure. While many methods exist for such measurements, (BET, porosimetry, etc.) they all suffer from some disadvantages. As will become clear from later discussion, water vapour penetration of the scale and its interaction with pores are important features of the reaction so that there is a clear need to obtain definitive data on the permeability of oxide scales. Recent work of Anghel et al. [80] using gas phase analysis of desorbed nitrogen and water suggests that further progress can now be made. Water is preferentially adsorbed on the pores walls and nitrogen then fills the remaining space. By analysis of the water/nitrogen ratio and amount upon desorption into ultra high vacuum, the pore size can be calculated.

3.3. Grain size

There is very little information about oxide grain size of scales grown in moist and dry atmospheres, however, Jacob et al. [18] comment that chromia formed on chromium at 800 °C and 1000 °C in dry N_2/O_2 mixtures has a larger grain size than when formed in the moist gas mixture (see Fig. 10). The effect was much more noticeable at the higher temperature. They attributed the observed increase in scale plasticity in the moist gas mixture to the smaller oxide grain size. It is of interest to note that in Ar/N_2 mixture the presence

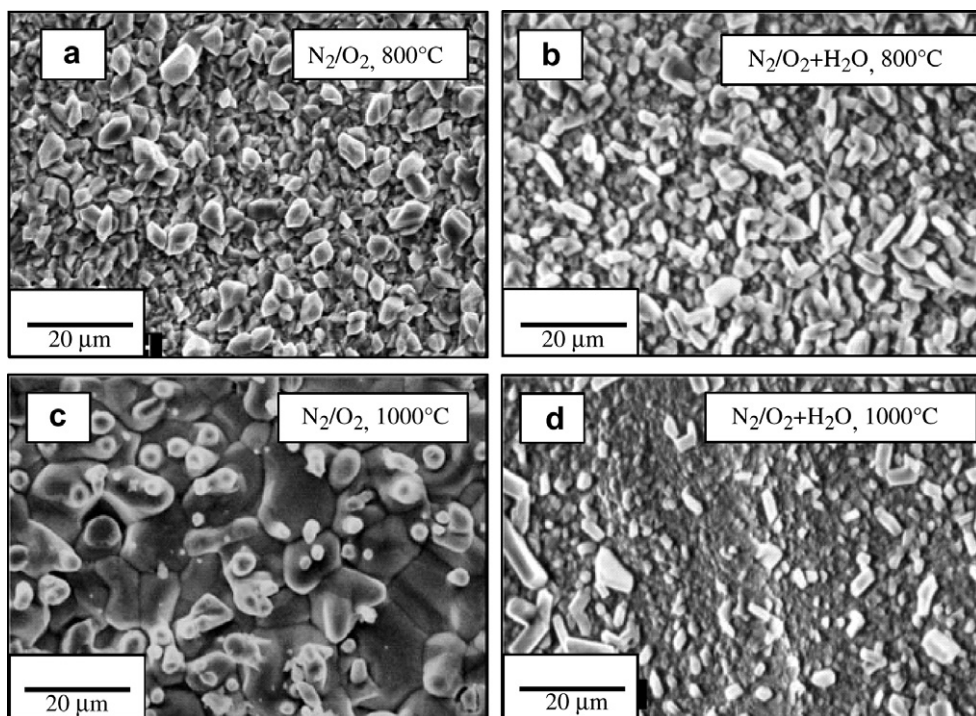


Fig. 10. Scanning electron micrographs of the surface morphologies for chromium after isothermal oxidation for 150 h at 800 °C (a,b) and 1000 °C (c,d) in N_2/O_2 (a,c) and $\text{N}_2/\text{O}_2/\text{H}_2\text{O}$ (b,d), after Ref. [18].

of water vapour had no effect of the oxide grain size. They proposed that nitrogen inhibited the reaction of water, but did not explain how this caused the observed changes in grain size.

4. Thermochemistry

Two important thermochemical considerations that determine the type of scale that forms are the relative stabilities of the oxides or hydroxides that could form and their vapour pressures. These two aspects are considered below:

4.1. Corrosion product stability

At one extreme, the stability of oxides in pure steam should be considered. Davies and Dinsdale [81] used MTDATA [82] to calculate the equilibrium $p(\text{O}_2)$ of pure steam at different operating pressures related to current technology of steam turbines and showed that, for example, all the oxides of iron were stable in this environment (Fig. 11). It is important to note that traces of hydrogen in the gas mixture can have a dramatic effect in lowering the $p(\text{O}_2)$ of the gas mixture, as first proposed by the early work at CERL [83] and confirmed by the work of Żurek et al. [25] where, for example, the presence of 1 ppm H_2 in an Ar 4% H_2O gas mixture would be sufficient to destabilise haematite (Fig. 12) while small amounts of oxygen would have the opposite effect (compare Figs. 11 and 12). In many other technically relevant situations water vapour is mixed with

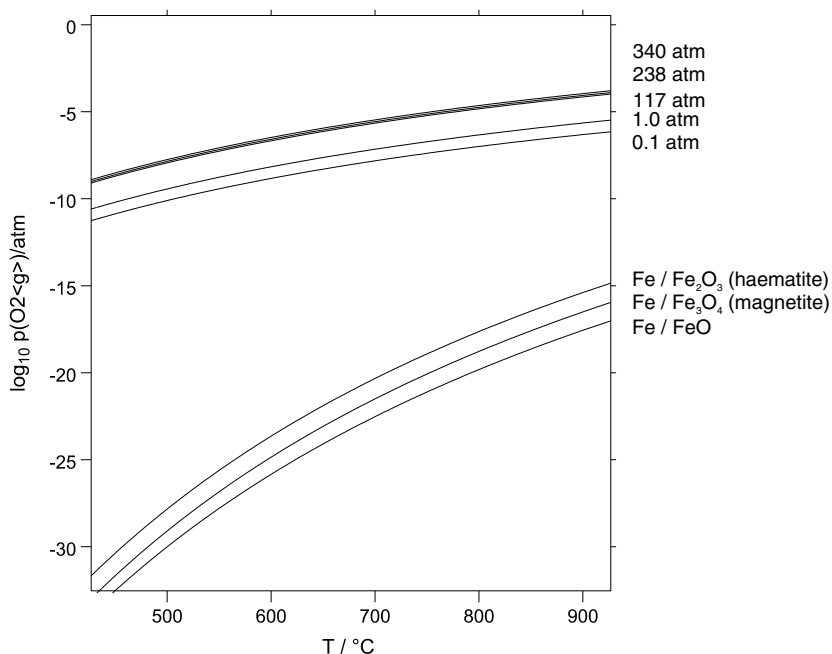


Fig. 11. Calculated oxygen partial pressure in equilibrium with steam at various pressures, and the calculated oxygen partial pressures required to form different iron oxides, after Ref. [81].

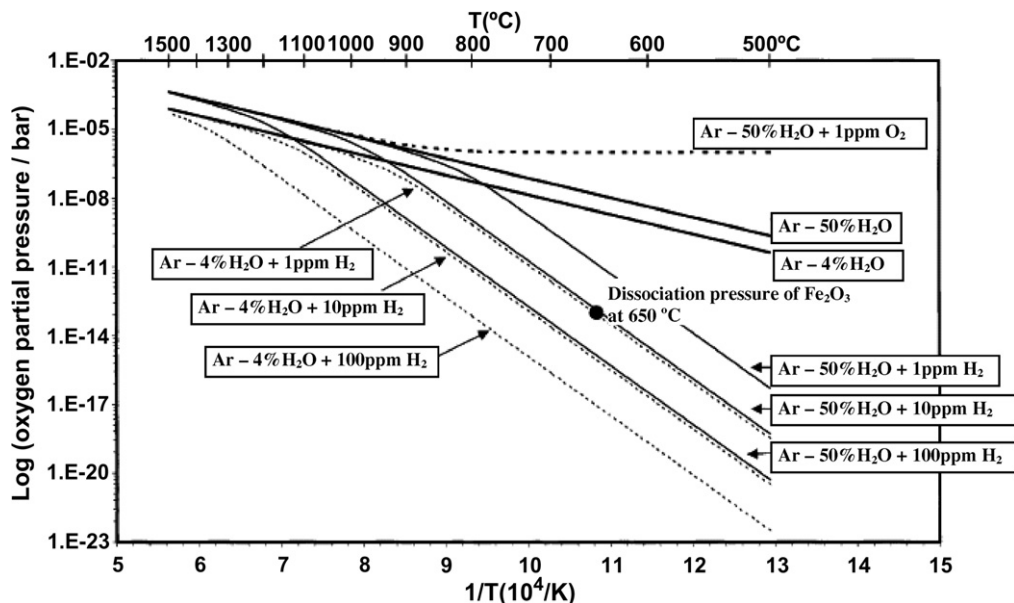
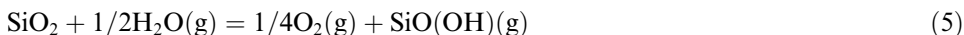
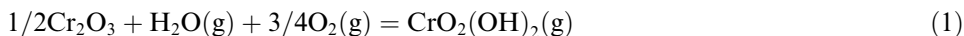


Fig. 12. Calculated oxygen partial pressures in various Ar H₂O H₂ gas atmospheres related to the dissociation pressure of Fe₂O₃ at 650 °C, after Ref. [25].

reducing gases or combustion gas mixtures so that the oxide stability will be determined by the equilibrium partial pressures of the particular mixture and it is necessary to ascertain the stability of possible oxides or hydroxides for the particular gas mixture of interest.

4.2. Volatile reaction products

Opila [58] recently completed a comprehensive review on the volatility of the three technically important oxides as hydroxides, i.e. alumina, chromia and silica involving the following reactions:



It was shown that where competition exists between growth and volatilisation a simple Tedmon model [84] in which the overall rate of metal wastage is a function of the parabolic rate constant for oxide growth and the linear rate constant for volatilisation is adequate to account for the observed kinetics. Various data sets exist for vapour pressure data of these hydroxides and in the case of CrO₂(OH)₂ these do not agree, but nevertheless Opila [43] showed that rates of evaporation increase in the following order: Al(OH)₃ < Si(OH)₄ < CrO₂(OH)₂ as shown in Fig. 13. It can be seen that the reaction products of

water vapour with chromia and silica have significant volatility at temperatures above about 800 °C, whereas for alumina temperatures in excess of 1400 °C are required.

The considerable body of work by Johansson and co-workers [37–41] convincingly demonstrates that in high $p(\text{O}_2)$ atmospheres containing water vapour loss of chromium by volatilization is a major factor in determining breakdown of protection for a number of austenitic steels. In their studies they show many examples of local breakdown of the protective chromia scale at the centre of the metal grain structure, with protection was maintained at the metal grain boundaries where the diffusion rate of chromium is sufficiently high to maintain protection. Johnson and Panas [85,86] calculated the stability of the different chromium hydroxides and confirmed that $\text{CrO}_2(\text{OH})_2$ is the most stable. Yamauchi et al. [42] carried out a series of experiments with sintered chromia exposed to $\text{N}_2\text{--O}_2\text{--H}_2\text{O}$ mixtures at 900–1200 °C at a constant flow rate of $2 \times 10^{-4} \text{ m}^3 \text{ min}^{-1}$, and demonstrated linear mass loss as expected and that the rate was dependent upon both the water and oxygen content of the gas mixture. $\text{CrO}_2(\text{OH})_2$ was the main volatile species and formed according to reaction (1) above, but it was proposed that at high temperatures (above about 1130 °C) the reaction may involve the trioxide as follows:



This suggestion is confirmed by an Arrhenius plot of chromia evaporation rates in water containing atmospheres showing that a different mechanism operated above about 1130 °C (Fig. 14).

The volatilisation of a number of possible products resulting from reaction of a P92 steel in oxygen water vapour gas mixtures at 650 °C was considered by Milewska et al. [87] as function of $p(\text{O}_2)$ but with a constant 10% water vapour. At low $p(\text{O}_2)$ 10^{-19} atm, the most volatile species are $\text{Fe}(\text{OH})_2$, $\text{MoO}_2(\text{OH})_2$ and $\text{WO}_2(\text{OH})_2$, but with increasing $p(\text{O}_2)$ up to 10^{-1} atm, $\text{MoO}_2(\text{OH})_2$ and $\text{WO}_2(\text{OH})_2$ remain the most volatile compounds but $\text{CrO}_2(\text{OH})_2$ and Mo_3O_9 also show significant volatility (see Fig. 15). Ehlers et al. [36] also proposed $\text{Fe}(\text{OH})_2$ as active volatile species in the oxidation of 9%

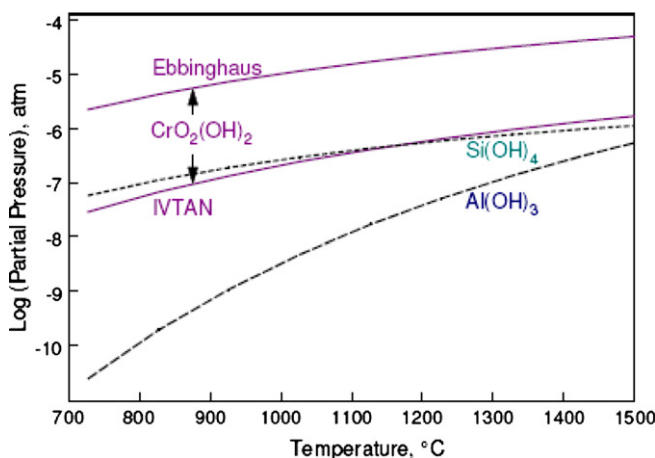


Fig. 13. Partial pressures of primary volatile species calculated for each oxide at 1 atm total pressure: 0.5 atm O_2 , 0.5 atm H_2O , after Ref. [43].

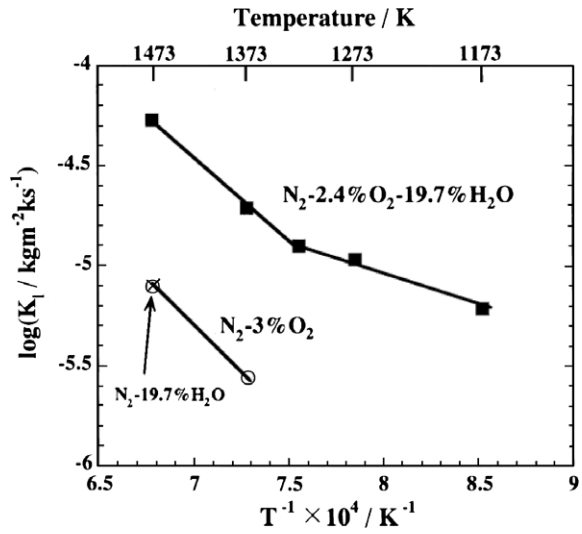


Fig. 14. Arrhenius plots of the evaporation rates of Cr_2O_3 in $\text{N}_2\text{-}3\%\text{O}_2$, $\text{N}_2\text{-}19.7\%\text{H}_2\text{O}$ and $\text{N}_2\text{-}2.4\%\text{O}_2\text{-}19.7\%\text{H}_2\text{O}$ atmospheres, after Ref. [42].

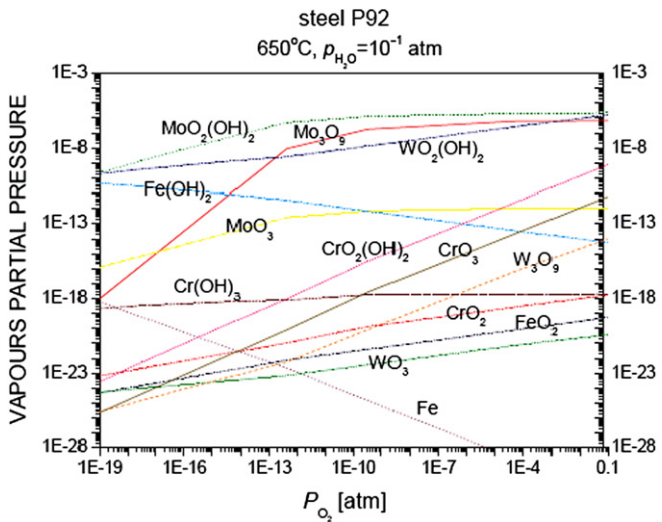


Fig. 15. Vapour pressures of the most important volatile compounds formed in the $\text{Fe-Cr-Mo-W-O}_2\text{-H}_2\text{O}$ system at $10^{-1} \text{ H}_2\text{O}$ and 650°C , after Ref. [87].

Cr steel in water vapour, but indicate that better data is required to confirm their suggestion. These results are also in general agreement with Davies and Dinsdale [81] who point out that in high pressure steam (341 atm) $\text{Fe}(\text{OH})_2$ is sufficiently volatile that it may be involved in the metal wastage process, but that at atmospheric pressure and 700°C the vapour pressure is only about 10^{-10} atm and thus would not be significant. The loss of

chromium from the scale by volatilization of $\text{CrO}_2(\text{OH})_2$ will also not have a significant impact on the corrosion process at these low $p(\text{O}_2)$ values, and in fact $\text{Cr}(\text{OH})_3$ is the most volatile chromium compound over the entire temperature range but the vapour pressure at 700 °C, for example, is only about 10^{-13} atm. Saunders and McCartney [88] using MTDA-TA [82] show that $\text{CrO}_2(\text{OH})_2$ becomes the dominant volatile species at 627 °C and 300 atm for $p(\text{O}_2)$ values greater than about 10^{-9} atm. Galerie et al. [23] confirm that at low $p(\text{O}_2)$ $\text{CrO}_2(\text{OH})_2$ does not possess sufficient volatility to be considered as a possible cause of breakaway oxidation of ferritic steels.

As suggested above, there is a need for improved data on volatilisation rates of the principle reaction products with water and oxygen in order to better predict behaviour. It is of interest to note, however, that while usually volatilisation effects are detrimental to long-term protection of engineering materials, at least one example was reported where it was claimed that the increased volatility of Mo compounds in the presence of water vapour helped establish a protective silica scale [60].

5. Oxide growth processes

Oxidation involves several processes occurring sequentially and concurrently; these are adsorption of the oxidant and, if ionic species are involved in oxide growth, dissociation, and diffusion of cations and/or anions through the growing scale. Diffusion of defects in oxides controls cation and anion transport, unless molecular diffusion of gases is involved. Also as will be seen in Section 6, the oxide is normally stressed during growth and when subjected to a thermal cycle one mechanism for relief of this stress is creep in either the substrate which is the more common, or the oxide. For creep to occur diffusion of defects must also take place. In the case of oxide growth, we are concerned with majority carriers as these are rate controlling, however for creep processes, since both anion and cation must move, it is the minority carrier that is rate controlling. There are three main creep mechanisms; grain boundary sliding, dislocation movement, and diffusion (Coble or Herring Nabarro). Diffusion creep is probably ruled out in most oxides since it only occurs at $0.7T_m$, so that the discussion will be mostly limited to the effects of water vapour on dislocation generation and movement.

We will also consider here transport processes other than lattice diffusion, short circuit paths by grain boundary diffusion or molecular diffusion for example, both of which can control or contribute to oxide growth, and again how these can be modified by the presence of water vapour. As will be seen, in some cases the details of the transport mechanism are often unclear, but nevertheless valuable information about the reactants involved and of their direction of movement in the growing scale can be obtained, particularly by use of $^{18}\text{O}_2/\text{H}_2$ ^{16}O experiments. The results of these studies will also be discussed.

5.1. Gas adsorption and dissociation

There is very little information in the “oxidation” literature related to the important first step in any oxidation reaction concerning gas adsorption and, where continued growth of the oxide is controlled by diffusion of cations and/or anions, the dissociation of the adsorbed molecule. Both adsorption and dissociation will depend on the catalytic activity of the surfaces, and as will be demonstrated, this can be significantly altered by the oxide defect structure and alloying additions.

5.1.1. General introduction

A useful starting point is to look at adsorption and dissociation mechanisms in general, and the following is taken from Henrich and Cox [89] and Masel [90]. In these references the bulk of the information refers to adsorption and dissociation processes at room temperature on single crystal specimens, where use can be made of surface science experimental methods. It is believed that the principles will apply to adsorption and dissociation of gases on oxide surfaces at high temperatures. Unfortunately there appears to be very little information about these processes at high temperatures.

Henrich and Cox [89] distinguish between dissociative and non-dissociative or molecular adsorption. For dissociative adsorption four types are considered:

- Weak electrostatic or dispersion (implies physisorption).
- Acid/base or donor/acceptor.
- Oxidation/reduction with electron transfer.
- Oxidation/reduction with oxygen transfer.

Generally chemisorption on oxides is different from that on metals due to the ionic nature of the surface and the involvement of lattice oxygen sites. Cation sites are Lewis acids and may interact with electron donor molecules such as water that has a lone pair of electrons, while oxide ions may act as basic sites interacting with acceptor ions such as a proton to produce a hydroxyl group. Lattice oxygen sites can simply react with an acidic molecule such as CO_2 forming CO_3^{2-} , or selective oxidation reactions can also be promoted. Where selective oxidation occurs, oxygen may be added to the adsorbate not as O^{2-} but as a neutral oxygen atom. There will be a corresponding reduction of the substrate in the form of electrons that might be free carriers, but more often this will lead to a localised decrease in the oxidation state of the metal at the surface. Stoichiometric surfaces are generally unreactive, and chemisorption, particularly dissociative adsorption, is promoted by surface defects and steps. The degree of “coordinative unsaturation” describes the extent of non-perfect coordination of the surface, and these unsaturated ions are able to act as acidic and basic adsorption sites, but are also bonded less strongly to the lattice so they can more easily be involved in oxidation/reduction reactions. These unsaturated sites may also have different electronic properties, so that these defects can also act as sources and sinks for electrons and further promote oxidation or reduction reactions.

As a guide to the reactivity of various gases of particular interest it may be useful to list their more important characteristics:

- **Hydrogen** is a non-polar molecule with low polarisability and has a weak donor or acceptor properties.
- **Water** has a large dipole moment and lone pair electrons and is therefore a good donor. Adsorption occurs by acid/base process with interaction with metal ions; non-dissociative molecular adsorption also occurs.
- **Carbon monoxide** has a small dipole moment and in spite of its lone pair electrons is a very weak donor.
- **Carbon dioxide** can act as a weak donor or acceptor.
- **Oxygen** is a very powerful electron acceptor and can be reduced in several steps.
- **Nitrogen** and **Argon** are generally inert as expected.

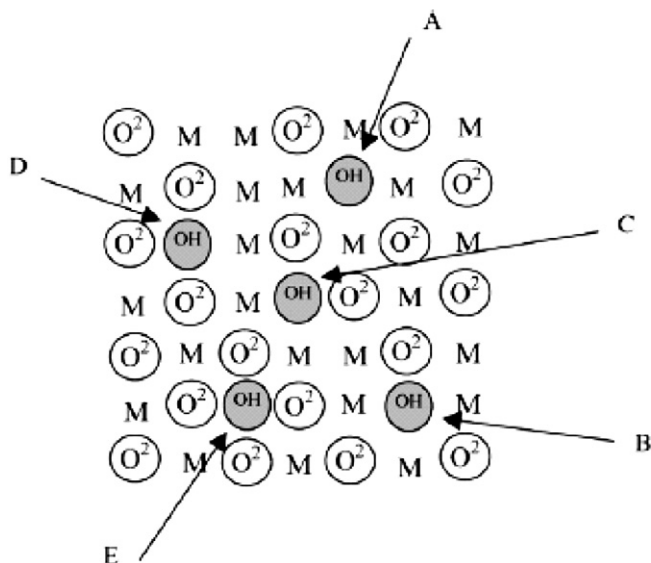


Fig. 16. Sites of different acid–base strength, from A to E the sites become more basic and less acidic, M denotes metal ions below the surface, after Ref. [91].

Additionally, from Mansel [90], acid–base reactions are further elucidated. He distinguishes between hard and soft acids and bases.

- A hard acid is an acceptor with a small affinity for electrons which remains charged during a reaction, for example, solvated H^+ , Al^{3+} , surfaces of alumina and silica.
- A hard base is a donor with no high lying donor orbitals, so that it has little capacity to donate electrons, for example H_2O , OH^- , and surfaces of MgO and TiO_2 .
- A soft acid readily accepts charge and generally has a high affinity for electrons with high polarisability to easily form covalent bonds, for example Pt^+ and Ag^+ .
- A soft base readily gives up charge with high polarisability and can easily form covalent bonds, for example, most metal surfaces.

Hard acids/hard bases interact strongly with each other, for example water dissociates on silicon at 100 K, but CO and H_2 do not adsorb on silicon at this temperature. Generally water has a higher hardness than most other species and adsorbs on most oxides.

5.1.2. Acid–base determination

There is a very large body of information about acid–base behaviour of oxide powders in the colloid science literature. At ambient temperatures acid–base characteristics of surfaces are usually determined by measurement of the point of zero charge (PZC) and or the iso-electric point (IEP). The PZC, or pH of a solution at which there is of zero charge, should not be confused with the isoelectric point (IEP), which also uses the pH scale and is the pH at which a powder does not move when an electric field is applied in a given suspension. The PZC and IEP can differ when, for example, multivalent metal ions, which adsorb specifically on the surface, are present.

In colloid science the IEP describes the ability of the surface hydroxyl groups to attract protons. Because of surface heterogeneity, the hydroxyl groups are in fact not equally acidic or basic [91]. Their functionalities are affected by the number, species and position of ions surrounding them. For example, as shown schematically in Fig. 16, site A is the most acidic because it is surrounded by four metal cations. A large portion of the electron density of the oxygen at site A is shifted to surrounding cations, and only a little is left for the bonded proton, making it easy for the site to lose a proton. Site E is the most basic because it is surrounded by four oxygen anions. The oxygen at site E is thus able to provide more electron density to an electron acceptor, making this site easy to adsorb an extra proton. Each of these sites has a different equilibrium constant with water and the surface as a whole acts as a weighted average of these sites.

Pinzari et al. [92] have demonstrated using acid–base contact angle titration measurements that titania produced by thermal oxidation has the same IEP as that for TiO₂ powders, of about 6. This gives some justification for using PZC/IEP values obtained from the field of colloid science to rank the acid–base nature of thermally grown oxides.

Sun and Berg [93] reviewed methods of measuring IEP. The choice of technique and scale for acid/base characterization depends on the specific application. For the cases in which the overall acid/base property is of interest, IEP (by electrokinetic titration) and H_{0,Max} (by indicator dye adsorption) are appropriate. For the cases in which the absolute acid/base property is of interest such as in the study of adhesion, it is more pertinent to use chemical shift (by XPS) and the heat of adsorption of probe gases (by calorimetry or IGC).

Point of zero charge (PZC) measurements also provide a means of determining the relative acidity and basicity of oxides and Kosmulski [94–96] lists such values for many oxide systems. A high PZC surface shows more basic functionality compared with its acidic functionality, whereas a low PZC surface shows more acidic functionality compared with its basic functionality. The value of the pH, where the concentration of negatively and positively charged surface groups is equal, is termed the PZC and is a property of the chemical groups on the surface of a material. The pristine PZC is obtained when inert electrolytes are used and the oxide material is free of specific adsorption. Various methods are used to determine the PZC;

- CIP (common intersection point of potentiometric titration curves obtained at three or more ionic strengths).
- Intersection (intersection point of potentiometric titration curves obtained at two ionic strengths).
- pH (natural pH of a dispersion).
- IEP (isoelectric point obtained by classical electrokinetic methods).
- Acousto (isoelectric point obtained by the electroacoustic method).

The values listed in the references were obtained by the different methods often do not agree, but Kosmulski suggests that confidence should be placed in matching values obtained by different methods. The relatively new electroacoustic method is believed to be free from many problems related to surface adsorption. It should be emphasized that the data are obtained at room temperature, and thus care should be taken in extrapolating to oxide scales formed at high temperature. Table 3 is attempt to extract the more reliable data from the compilations produced by Kosmulski and hopefully gives some indication

Table 3

Selected points of zero charge (PZC) of various oxides taken from Kosmulski [95,96]

Oxide	PZC/IEP	Method
α -Al ₂ O ₃	9, 8.9, 9.3 , 9.3 , 9	IEP, IEP, Acousto, CIP, IEP
γ -Al ₂ O ₃	9.3, 9.2 , 9.3 , 8.6,	IEP, IEP, Ph, Acousto,
CeO ₂	6, 7.3, 11.2	IEP, IEP, Acousto
Cr ₂ O ₃	4, 6.7 (5.2)	pH, pH, (pH Ref. [97])
CuO	6.9–8.5	pH, Intersection, IEP
Fe ₂ O ₃	7.6 (average of 11 – range 6.3–8.5), [9]	IEP, CIP, pH, [Acousto]
Fe ₃ O ₄	6.5, 8 , 7.9	Intersection, IEP, CIP
MnO ₂	4.2–6.8	IEP (depends on electrolyte, probably not inert, values uncertain)
NiO	7.8, 8.1, 9.5	IEP, IEP, CIP
TiO ₂ (rutile)	5.2 , 5.3 , 5.7, 5.8	Acousto, IEP, Acousto, Acousto
SiO ₂	2–4 (if any)	IEP, Ph, Acousto
Y ₂ O ₃	7.9, 8.5 , 8, 8.5	CIP, IEP, IEP, Acousto
ZrO ₂	6.5 , 7 ± 0.3, 8.2, 6.4	IEP, IEP, IEP, Acousto
ZrO ₂ –8%Y ₂ O ₃	6	IEP

The matching CIP and IEP recently found for magnetite [8] are substantially higher than most previously reported PZC for Fe₃O₄. Very likely the previously reported PZC of magnetite were underestimated; namely, one expects higher PZC for lower oxidation states [1,9]. Thus, the pristine PZC of magnetite should be higher than that of hematite.

of the relative acidity/basicity of oxides and hence their affinity towards water. Those values which are in bold font are believed to be the more reliable. Some more recent data on plasma sprayed chromia powders have been obtained by Harju et al. [97] and these are also included in the Table.

5.1.3. High temperature behaviour

A significant contribution to the understanding of adsorption and dissociation processes at high temperatures has come for the research group at Kungliga Tekniska Högskolan, Stockholm. Hultquist and co-workers have used a novel technique in which the oxidation process is studied by analysing gas consumption and evolution in a sealed volume by isotope labelling methods during the course of the oxidation reaction. The main results of their work are summarised below.

Anghel et al. [98] studied the adsorption of N₂, H₂, CO and H₂O on oxidised chromium and zirconium and zirconium metal in the temperature range 400–600 °C. The dissociation rate of CO varies by a factor of 10⁴ between materials studied. It was found that upon addition of water to the CO gas, the dissociation rate of CO on Cr decreased which can be interpreted as a blocking effect by water. It was also found that upon subsequent removal of water from the gas phase the CO dissociation rate increased again. It is shown that the surface activity for CO dissociation should be a key factor for carbon uptake in certain applications and can be reduced by adsorbed water. Based on the results of this work, the following ranking for the tendency of adsorption at high temperatures is made: N₂ < H₂ < CO < H₂O, which is broad agreement with molecular characteristics listed above.

Oxygen dissociation rates can be greatly altered depending on the active surface as exemplified by rates on platinum, yttria and alumina [99]:

- Pt at 900 °C: 2000 $\mu\text{mol O cm}^{-2} \text{h}^{-1}$.
- Y_2O_3 at 900 °C: 365 $\mu\text{mol O cm}^{-2} \text{h}^{-1}$.
- Al_2O_3 at 900 °C: approximately 3 $\mu\text{mol O cm}^{-2} \text{h}^{-1}$.

Furthermore Återman and Hultquist [17] showed that with an Fe 20%Cr 10%Al alloy oxidised at 920 °C water dissociation rates decreased with decreasing oxidation rates, and they interpreted this as the result of a fewer defects in the more mature alumina scale (Fig. 17). However, the oxygen dissociation rate was unaffected by the oxide defect structure. They also demonstrate that the partial dissociation of water into OH and H is faster than oxygen dissociation.

Hultquist and Szakálos [100] reported oxygen dissociation rates as a function of temperature on a number of different metallic and oxide materials in the temperatures range 200–800 °C (see Fig. 18). These data suggest that, when extrapolated, at increasing temperatures dissociation rates become less dependent upon the surface chemistry, but even so dissociation rates on metallic materials are between one and two orders of magnitude greater than the most active oxide (yttria) at 1000 °C.

Åkermark studied [101] the oxidation of Kanthal AF, an alumina-forming alloy, at 920 °C and silicon at 950 °C in oxygen water vapour gas mixtures using $^{16}\text{O} + \text{H}_2^{18}\text{O} + \text{H}_2^{16}\text{O}$ at a total pressure of about 20–30 mbar. The oxidation reactions and oxygen exchange mechanisms were studied by monitoring the concentration of consumed and evolved gases in a sealed volume with mass spectrometry. He demonstrated that very few of the molecules hitting the surface participate in oxidation and in oxygen exchange, which indicates that there are only a few active sites on the surface. For silicon, oxidation rates were increased by small additions of water vapour and Åkermark concluded that atomic oxygen was the dominant diffusing species. An addition of 0.6% Y to Kanthal AF alloy increases the oxidation and oxygen-exchange rates by a factor of about 2. This is most likely due to the fact that Y increases the O_2 dissociation rate and, thereby, the surface concentration of atomic O. Therefore species with a high affinity to generate active sites can have a large impact on reactivity even in the parts per million range. This could

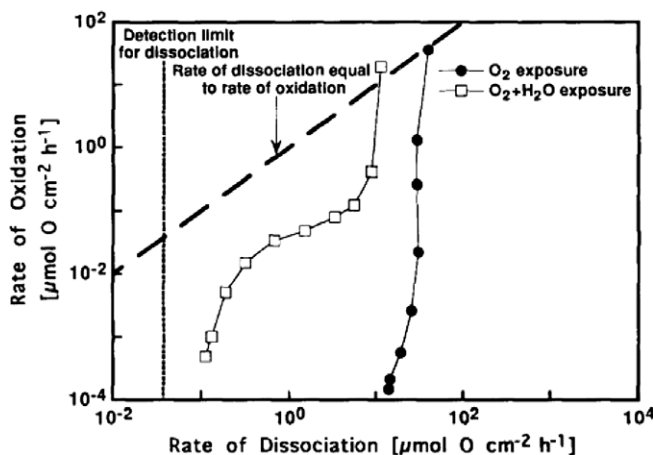


Fig. 17. Oxidation rate of an Fe 20%Cr 10%Al alloy at 920 °C versus dissociation rate in 7.5 mbar O_2 and water dissociation rate in 6 mbar O_2 and 14 mbar H_2O , after Ref. [17].

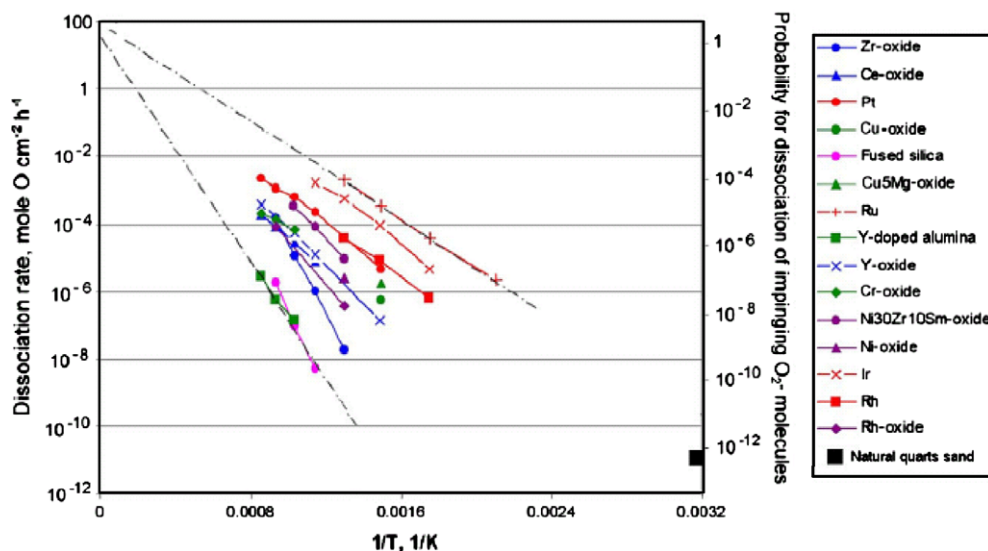


Fig. 18. Dissociation rates in 20 mbar O_2 versus $1/T$ on different materials and corresponding probabilities for dissociation, after Ref. [96].

explain the effect Y has on oxidation of Kanthal AF and why H_2O in O_2 increases the oxidation rate of Si.

Åkermarck discussed [101] oxygen exchange mechanisms involving adsorption and/or dissociation that have been thoroughly evaluated in the literature; there are three main paths:

- association of two O_2 to O_4 and then dissociation back to two O_2 ;
- association of one O_2 and one surface adsorbed $\cdot O$ to O_3 ($\cdot OO_2$). The O_3 will then dissociate to O_2 ($\cdot OO$) and $\cdot O$ and
- association of two surface-adsorbed $\cdot O$ to O_2 .

In (i) no O_2 dissociation is needed. It is not possible to measure this path in an $^{16,16}O_2 + H_2^{16}O + H_2^{18}O$ gas mixture, but a non-statistical distribution of isotopes in O_2 is required (for instance $^{16,16}O_2 + ^{18,18}O_2$), which is not the case. In (ii) and (iii) the adsorbed O can have two sources: the gas (O_2 and H_2O) or the oxide (oxygen exchange with the oxide). In the $^{16,16}O_2 + H_2^{16}O + H_2^{18}O$ gas mixture, paths (ii) and (iii) are operative, which sometimes can be evaluated from the initial increase of $^{16,18}O_2$ and $^{18,18}O_2$. In this type of evaluation, an important question to resolve is whether $^{16,18}O_2$ an intermediate in the formation of $^{18,18}O_2$. In any case, the surface-adsorbed O in paths (ii) and (iii) must come from dissociation of O_2 and H_2O . An initial increase of $^{18,18}O_2$ is due to path (iii) and the surface-adsorbed O comes from complete dissociation of H_2O .

O_2 dissociation has a higher activation energy on diamonds than water, thus dissociation of water is favoured at low temperature and O_2 dissociation at high temperatures [102].

In gas mixtures one also needs to consider the effects of competitive adsorption and dissociation, and Raynaud and Rapp [76] in a study of whisker formation on copper at 500 °C and nickel at 1100 °C demonstrated that whisker formation was promoted by

the presence of the addition of water to oxygen. Whiskers are believed to be formed at dislocations in the oxide [103] and have hollow cores such that rapid surface diffusion within the whisker can take place and their growth is then limited by the availability of oxidant at the whisker tip. Raynaud and Rapp [76] propose that the faster growth of whiskers in moist atmospheres is related to the generally faster dissociation of water molecules than for most other oxidant molecules. The observation of whisker formation, particularly at lower temperatures, is often associated with the presence of water vapour, for example, see also the work of Pieraggi et al. [32] and Monteiro et al. [33], and it is believed that the mechanism proposed by Raymond and Rapp [76] has general applicability.

In conclusion, while a large amount of information exists about adsorption and dissociation processes derived from surface science studies at low temperatures (room temperature or below), very little direct evidence exists about these processes at temperatures of interest to researchers concerned with high temperature corrosion. Some very interesting observations have been made using isotopic labelling methods of gas chemistry in sealed systems where oxidation reactions occur, and to some extent these experiments have supported the findings of surface science studies at much lower temperatures. In general, it appears that dissociation of any gas molecule is favoured by defects in the surface, and thus the stoichiometric oxides such as alumina may therefore be less active than, for example, FeO. Dissociation of water seems to be more rapid at lower temperatures than for example oxygen, but this difference may be less pronounced at higher temperatures.

There seems to be general agreement that relative acidity/basicity of oxides controls the reaction with water vapour, where water vapour will react more strongly with more acidic oxides. However what is not clear is how to rank oxides. The commonly used method of PZC or IEP is believed to yield a good relative assessment while use of chemical shift measurements by XPS or heats of adsorption by calorimetry or gas chromatography yield better absolute values [93]. The use of PZC or IEP data in Table 3 provides some evidence in support of this concept. Considering the results presented in Section 2 of this review it was demonstrated that materials forming α -alumina and NiO scales were generally unaffected by the presence of water vapour as expected from the high PZC (9.3 and 7.8–9.7, respectively) while chromia, titania and silica are all affected by the presence of water vapour and have more acid PZC values (4–6.7, 5.3 and 2–4, respectively). However Galerie et al. [23] compared chromia and haematite PZC measurements and concluded that haematite is more acidic than chromia (although the data in Table 3 suggests the opposite). In agreement with this, for an Fe 15%Cr ferritic steel oxidised in Ar water vapour mixtures at 800–1000 °C growth rates of haematite were about 3 times higher than chromia at 800 °C. It was therefore concluded that, when competition occurs between these two oxides on the steel surface, at a crack tip or in an interfacial pore, haematite is favoured in the presence of water vapour, leading to nodule formation and catastrophic oxidation. Furthermore, Mansel [90] lists Al^{3+} , surfaces of alumina and silica as being hard acids and thus reaction with water vapour would be expected. It is clear therefore, that further clarification of oxide scale basicity is required and that the PZC may not be the most appropriate measurement in order to rank behaviour.

5.2. Lattice diffusion

In this section we will consider how the presence of water vapour affects the diffusion of both majority and minority defects in oxides of interest. To fully understand the effect of

water vapour on defect dependent properties it is necessary first to consider oxide transport processes in the absence of water vapour. The three main protective oxides will be considered, (alumina, chromia and silica) as well as the iron oxides and nickel oxide. The work of Kofstad [71,104–106], Norby [107] and Atkinson et al. [108] has been used to provide the basic information on these systems. Dieckmann [109] reviewed the transport of water in oxides but importantly also considered solution of water in oxides.

Before starting a description of the defect structure in these oxides it may be helpful to briefly remind the reader of the common defects in stoichiometric and non-stoichiometric oxides. For stoichiometric oxides, Schottky defects occur when there are equivalent concentrations of anion and cation defects, normally anion and cation vacancies, and Frenkel defects, which occur when an anion or cation lattice site is transferred to an interstitial site leaving a cation or anion vacancy (anion Frenkel defects are also referred to as anti-Frenkel defects). For non-stoichiometric oxides, four cases can be considered:

- (i) oxygen deficit, an oxygen vacancy is created and electroneutrality is maintained by the presence of two electrons on the vacant oxygen site;
- (ii) metal excess, interstitial metal ions are formed and charge neutrality maintained by a reduction in the oxidation state of that normal for the cation on metal lattice sites;
- (iii) oxygen excess, an interstitial oxide ion is created and electroneutrality maintained by the creation of electron holes;
- (iv) metal deficit, metal vacancies are formed and electroneutrality maintained by the creation of electron holes at that vacant site.

(i) and (ii) above are examples of n-type semiconductivity in which there are charged oxygen vacancies and/or metal interstitials and (iii) and (iv) p-type where there are charged oxygen interstitials and/or metal vacancies. For materials with high concentrations of defects, these can become associated as clusters (see, for example, discussion of the FeO defect structure in Section 5.2.4). Whereas simple defects can be treated as ideal solutions, this is not the case for clusters and thus the quantitative understanding of transport in these cases is more complex and in some cases still not fully understood.

Kroger and Vink [110] developed a helpful notation that is commonly used to describe these point defects and this is used in what follows. When a metal ion occupies a metal lattice site this is written M_M , and likewise an oxygen ion on a normal oxygen site is written O_O . Correspondingly, vacancies are written V_M and V_O and interstitials M_i and O_i . Most oxides contain impurities, and these are written, for example in the case of iron in chromia, as Fe_{Cr} or Fe_i if the iron ion occupies a chromium lattice or interstitial site, respectively. Charges on the site are written as net charges. Thus a vacancy on a metal lattice site has no effective charge if the electrons remain trapped at the cation site and it is written as V_M^x but if the vacancy is ionised and has a net doubly positive charge it is written V_M^{2+} . Electrons and holes have effective negative and positive charges, respectively, and are written e' and h' . If an electron, for example, is associated with a normal cation site it can be considered as a valence defect and it is written as M_M' .

A helpful review by Norby [107] describes of the possible effects of hydrogen/water vapour incorporation of the transport properties of oxides and how these might affect high temperature oxidation. The literature demonstrates that hydrogen dissolves as protons and is bound to oxide ions to form the substitutional hydroxide $(OH)_O^\bullet$. These defects may equivalently and more simply be described as interstitial protons, $H_i^\bullet$. Generally it

is found that the concentration of $H_i^\bullet$ increases with $p(H_2O)$ and decreasing temperature. The dissolution of protons in an oxide can be written thus:



or by considering gas equilibria



Thus at sufficiently low $p(H_2O)$ or $p(H_2)$ protons are a minority defects. The concentrations of native defects are independent of $p(H_2O)$ or $p(H_2)$ (at constant $p(O_2)$), while the concentrations of protons increase with $p(H_2O)^{1/2}$ or $p(H_2)^{1/2}$. At higher $p(H_2O)$ or $p(O_2)$ protons may become the dominant defect, compensated for by defect electrons, metal vacancies, oxygen interstitials or acceptor dopants. Many investigations focus on the equilibrium between water vapour, oxygen vacancies and protons as being the most likely:



which, in general, is exothermic so that protons are dominant at low temperatures and oxygen vacancies at high temperatures. It is also important to consider the parallel reaction of dissolution from the gas phase:



Thus different types of hydrogen-containing species may be present simultaneously, i.e. molecular water and OH groups, as is frequently found in glasses (silica, for example). In close packed structures such as the alumina and chromia, dissolution of molecular water would be less favoured.

Fig. 19 shows how the defect concentration in M_2O_3 (where M is any trivalent metal) changes as a function of $p(H_2O)$ for a constant $p(O_2)$. It can be seen that at high $p(H_2O)$ metal vacancies are generated and, thus for an oxide growing by cation diffusion, oxidation rates would be expected to increase. The concentration of protons is increased by acceptor doping and decreased by donor doping, so that it is possible to use acceptor doping to enhance hydrogen transport in oxides, and conversely, to use donor doping to reduce it.

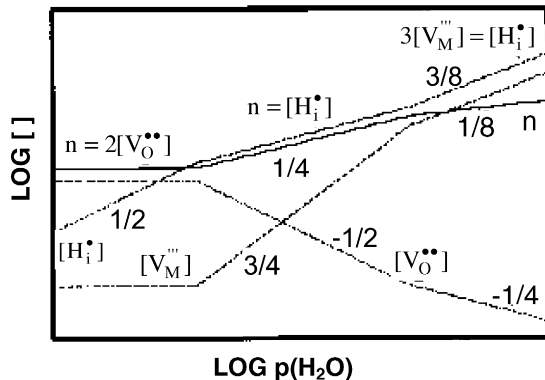


Fig. 19. Example of defect concentrations in M_2O_3 versus water vapour partial pressure at constant $p(O_2)$; numbers along lines denote slopes, after Ref. [107].

It is generally agreed that the Grotthuss mechanism allows transport of “water” in oxide scales by a proton “hopping” process, in which protons localised at oxide ions move by transfer from one oxygen to another. Since oxygen is available everywhere the net effect of proton diffusion is diffusion of water, and since proton diffusion rates are high compared with metal or oxygen, diffusion of “water” is easy.

Norby [107] concludes his review with the comment that although the general principles of the effects of protons can be outlined, at that time (1999) the uncertainties regarding transport in the oxides scales of interest were such that it was not possible to predict with any certainty the effects of water vapour on lattice transport. In the following, discussion of lattice diffusion will be limited to consideration of alumina, chromia, silica, iron and nickel oxides.

5.2.1. Lattice diffusion in alumina

The general features of the development of an alumina scale are agreed. The scale forms by diffusion of oxygen via grain boundaries and counter diffusion of aluminium, so that new scale forms within the scale. This leads to a build up of stress and usually the scale buckles and eventually spalls. The well known effect of rare earth additions in improving the adherence of alumina is the result of changing the transport in the scale to one that is predominantly by diffusion of oxygen inward [71]. Hultquist et al. [99] have suggested that atomic oxygen is the primary diffusing species.

There remains some doubt about the intrinsic (naturally occurring) defects in α -Al₂O₃ although it is generally believed to have negligible non-stoichiometry [108]. Experimental and theoretical studies concerning the dominant intrinsic disorder are found to be inconclusive, but where a preference is stated it is for Schottky disorder. All studies agree however that the cation Frenkel process is of sufficiently high energy as not to play an important rôle. Thus, it seems impractical to distinguish between Schottky and anion Frenkel processes and it is likely that the conclusion of El-Aiat and Kröger [111] which states that it is not possible to differentiate, categorically, between these mechanisms, is probably valid.

Atkinson et al. [110] modelled the solution of aliovalent and isovalent ions in α -alumina, and conclude that while solution of most impurity ions that have a relatively large ionic radius compared with Al³⁺ is difficult, because of the small intrinsic defect concentration, impurities will dominate transport processes. Larger isovalent ions such as Y³⁺ will dissolve in α -alumina, and while not changing the defect structure *per se* will tend to concentrate at the grain boundaries and form second phase material and thus alter transport in the oxide by “opening” the grain boundaries to provide diffusion paths for the transport of oxygen as is in fact found [112].

In a study of the conductivity of single crystal α -alumina in wet hydrogen between 1100 and 1500 °C, containing a number of different impurities but none in excess of 10 ppm, El-Aiat and Kröger [111] concluded that while hydrogen dissolves in α -alumina much of it is immobile, but the oxide changes from p-type to n-type conductor with mixed electronic ionic conduction by e^- , h^+ , $[V_{Al}^{'''}]$, $[Al_i^{''}]$ when hydrogen dissolves. They propose that H_i^- and H_i^+ are the mobile minority species and H_i^x an uncharged mobile species may be a majority carrier. The concentration of hydrogen in the oxide increases with an increase in the temperature used to saturate the oxide, the partial pressure of hydrogen used and the $p(O_2)$ or $p(H_2O)$. Proton conduction was observed by Kurita et al. [113] in a range of impurity polycrystalline doped α -aluminas in the temperature range 1000–1400 °C at

low $p(\text{O}_2)$, but not at high $p(\text{O}_2)$, although they did not identify the mobile species. Fukatsu et al. [114] concluded that at 1100 °C in 20% H_2O 1% H_2 Ar gas mixture a Mg-doped α -alumina single crystal reversibly incorporated hydrogen as an interstitial proton, and that this the proton was found to be a charge carrier at high temperatures. Norby and Kofstad [115] also reported proton conduction in a polycrystalline sintered α -alumina under reducing conditions.

Thus it seems, that while the evidence is quite strong that protons dissolve in α -alumina, the effect on ionic transport is less clearly defined. Oxide growth is controlled by grain boundary of oxygen and, in the absence of rare earth additions such as yttrium, some outward diffusion of aluminium is believed to also occur [71]. It is not known how or whether protons will affect grain boundary diffusion, and again there seems to no evidence that cation transport is greatly affected by proton dissolution, although from Fig. 19 an increase in cation vacancy concentration in p-type semiconductor would be expected with increasing proton solution. This result is in general agreement with the results presented in Section 2.1 where it was reported that water vapour had little effect on the oxidation rate of α -alumina-forming alloys although adhesion may be reduced. It was reported that the early stages of oxidation were affected by the presence of water vapour, and although proton hopping has been observed [116] with γ -alumina at modest temperatures the authors did not discuss the effects on cation or anion transport, and there seems little information about the other transition aluminas. In terms of creep processes, we need to consider bulk diffusion and here we would expect that oxygen diffusion would be rate controlling, and introduction of protons into the lattice would reduce the oxygen vacancy concentration $[\text{V}_\text{O}^\times]$ and thus inhibit creep. However, the OH^- mobility is increased and thus creep rates could be enhanced.

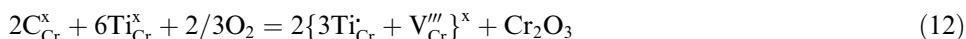
5.2.2. Chromia

The extent of non-stoichiometry in chromia is very small, but unfortunately there are no reliable quantitative data. The general features of chromia formation are similar to that described α -alumina, but in this case the outward diffusion of chromium is more important than inward diffusion of oxygen, so that growth of new oxide occurs in the outer part of the scale. The improved oxide adhesion when rare elements are present is again ascribed to a change in the transport properties such that oxygen grain boundary diffusion is favoured. It is also proposed that segregation of the rare earth elements to the oxide grain boundary prevents grain growth and thus enhances oxide plasticity [71]. Galerie [117] has recently shown using $^{16}\text{O}_2/^{18}\text{O}_2$ or $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$ experiments that for a Fe 15%Cr ferritic steel at 800 °C the presence of water vapour also encourages inward growth.

Holt and Kofstad [118,119] reviewed the literature regarding defects and defect dependent properties of chromia such as electrical conductivity and self-diffusion. They also reported on an extensive study of the electrical conductivity at temperatures from 440 °C to 1500 °C. A major difficulty in studying and interpreting the results in detail is the extremely slow equilibration kinetics due to slow rates of diffusion of native point defects and cation dopants, and thus it is often only possible to obtain semi-quantitative results. They concluded that the oxide is an electronic conductor. At temperatures above 1000–1200 °C intrinsic electronic equilibrium predominates while at lower temperatures chromia is an extrinsic conductor due to the presence of dopants or unavoidable impurities. The observed transition temperatures from the high temperature to the low temperature behaviour at near atmospheric oxygen pressure depends on the impurity or dopant

concentration. When undoped chromia was exposed to a hydrogen/water vapour mixture, the conductivity was found to be independent upon both $p(\text{O}_2)$ and $p(\text{H}_2)$ at temperatures in excess of about 1000 °C, but dependent on $p(\text{O}_2)^{1/4}$ at lower temperatures where hydrogen dissolution becomes appreciable.

Holt and Kofstad studied chromia doped with 2 mol% of tetravalent Ti [105] and divalent Mg [106] at 1000 °C. For Ti-doped Cr_2O_3 , the oxide is an n-type conductor at reduced oxygen activities and a p-type conductor at high oxygen activities. This is qualitatively the observed behaviour (Fig. 20). Furthermore, at highly reduced oxygen activities the n-type conductivity is predicted to be independent of or exhibit a small oxygen pressure dependence, but as the oxygen pressure dependence is increased and when the dissolved titanium is compensated by chromium vacancies, the n-conductivity is predicted to exhibit a larger oxygen pressure dependence (and as a limit $\sim p(\text{O}_2)^{1/4}$). With a further increase in oxygen activity, somewhat unexpectedly, the oxide becomes a p-type conductor with a limiting oxygen pressure dependence of $p(\text{O}_2)^{1/4}$. However Atkinson et al. [120] also studied Ti-doped chromia but at much higher Ti additions (10–15 mol%) and observed only n-type conductivity with a $p(\text{O}_2)^{-1/8}$ dependence, although $p(\text{O}_2)^{-1/4}$ would be expected from a donor dopant such as titania, but this was attributed to slow equilibration kinetics. They demonstrated that even at these relatively high doping levels a solid solution with negligible change in unit cell volume was formed. The variation in measured density with Ti concentration is consistent with the Ti being dissolved as Ti^{4+} compensated by Cr vacancies. These observations agree with atomistic simulations of the solid solution which also indicate that the Ti^{4+} ions and Cr vacancies form complex defects of lower energy, as shown in Eq. (12) below:



Ti doping gives n-type semiconductivity due to a small concentration of Ti^{3+} in equilibrium with the complexes that donate electrons to the conduction band by ionisation to Ti^{4+} .

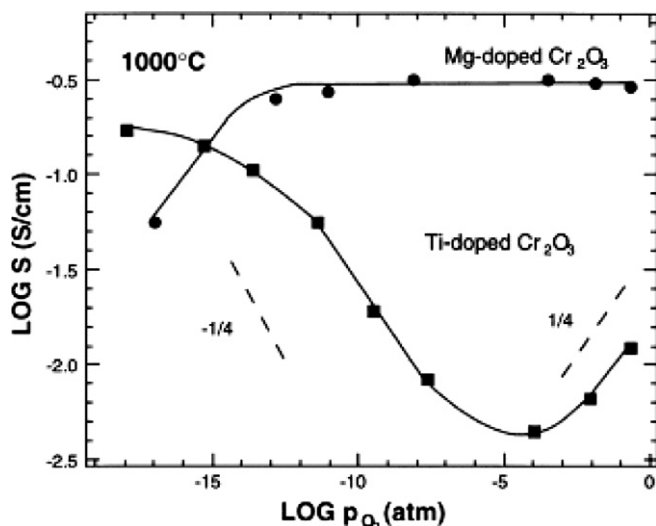


Fig. 20. The electrical conductivity at 1000 °C as a function of the partial pressure of oxygen for chromia specimens with additions of 2 mol% MgO and TiO_2 , respectively, after Ref. [105].

For MgO-doped chromia the opposite behaviour was observed: the oxide is a p-type conductor, and at high oxygen activities the dissolved MgO is compensated by electron holes and at reduced oxygen activities by oxygen vacancies (or in principle by chromium interstitials). The dependence of the electrical conductivity on the oxygen-activity is shown in Fig. 20. Hydrogen dissolves in both systems and the concentration increases with decreasing temperature. In the case of Mg-doped chromia, a p-type oxide, an increase in the proton concentration can result in either a decrease in positive holes and/or an increase in cation vacancies [28] as shown below:



For Ti-doped chromia Holt and Kofstad [105] did observe a dependence upon $p(H_2)$ and concluded that the solubility of hydrogen (water) was less than that in Mg-doped chromia, and thus it is not possible to predict any likely changes in ionic transport based upon conductivity measurements.

In summary therefore, there is clear evidence, as reported in Section 2.2, that the presence of water increases the oxidation rate of chromia formed on pure chromium [18–21], and on ferritic steels [28,29,35] where different atmospheres were used on the two sides of a sheet specimen simulating an interconnect in a SOFC [28,35] or a boiler tube [29] in which hydrogen was generated on one side of the metal specimen which was exposed to air on the other side. In all these cases, there is general agreement that the increased oxidation rate is the result of increasing the cation vacancy concentration to compensate for an increase in the concentration of the hydroxyl defect, (OH'_O) . In the case of the ferritic steels, it was also observed that iron diffusion was increased in the chromia scale.

It was reported [18] that chromia scales on pure chromium formed in water containing atmosphere appeared to be more plastic and that adhesion was improved [20], and it would seem that in terms of defect concentration the main effect of water vapour is to increase the concentration of the majority species so that there one might not expect to see an effect on creep rates. The improved plasticity in the presence of water vapour was believed to be the result of a smaller chromia grain size compared with that formed on chromia in dry atmospheres. But as noted by Galerie [117] inward diffusion in water containing atmospheres is encouraged, presumably by rapid diffusion of OH^- so that the diffusion of the minority carrier is thereby increased leading to the observed increase in scale plasticity.

5.2.3. Silica

Generally, engineering alloys containing silica are used at temperatures below about 1000 °C, and in this temperature range silica has a glassy structure so that its transport processes are very different from alumina and chromia discussed above. Formation of silica on silicon is by inward diffusion, so that oxygen must be transported through the silica scale. Deal and Groves established [51] that in the rather open network structure of glasses, molecular oxygen is the primary medium for transport of oxygen during formation of silica, whereas in water containing atmospheres molecular water is the dominant species resulting in an increase in the oxidation rate. This observation is somewhat surprising because the diffusion rate of water molecules is lower than oxygen in silica. However Deal and Groves point out that growth of silica is controlled by the equilibrium concentration, and the concentration of water molecules is three orders of magnitude greater than for oxygen.

There is little information about the transport processes in silica layers formed on engineering alloys, however, Wouters et al. [62] observed that a silica layer formed on a Fe

15%Cr steel in water containing atmospheres was less protective than when formed under dry conditions. They proposed that the OH groups diffusing through an outer chromia layer caused dissociation of the –Si–O–Si– network into less protective –Si–OH terminal groups and thus allowed easier transport of iron ions.

5.2.4. Iron oxides

Wüstite grows by outward movement of iron. It is a highly defect metal deficient oxide, $\text{Fe}_{1-\delta}\text{O}$, where δ varies between 0.05 at the iron wüstite boundary and 0.14 at the wüstite magnetite boundary depending upon the temperature and $p(\text{O}_2)$ [71,121]. It is important to note that the degree of non-stoichiometry decreases with increasing temperature at a constant $p(\text{O}_2)$ in contrast to most other non-stoichiometric oxides. The normal defect structure consists of clusters of iron vacancies and the simplest subunit known is a 4:1-cluster consisting of a trivalent interstitial iron ion, Fe_i^{3+} , tetrahedrally coordinated by four cation vacancies. Larger $m:n$ -clusters composed of m iron vacancies and n iron interstitials, e.g. the 13:4- or Koch–Cohen-cluster, can be formed by combining several 4:1-clusters., there are many other possibilities as discussed by Minervini and Grimes [122] who concluded that the 4:1 and 7:2 clusters are favoured at low defect concentration and that the 12:4 cluster (Lebreton–Hobbs) dominates at high defect concentrations; their work did not support the existence of the 13:4.

It will be recalled that when iron is exposed to moist atmospheres oxidation rates increase particularly at high temperatures ($>900^\circ\text{C}$) and that the plasticity of the FeO also increased [69,72], thus transport of both anion and cation were increased by the presence of water vapour. Based on the formation of $(\text{OH})^-\text{O}$ it is likely that an increase in cation vacancies would result, but it not quite so easy to understand the increase in plasticity by this mechanism. Rahmel and Tobolski [69] propose that oxygen transport is increased by the dissociative mechanism (see Section 5.2), while Tuck et al. [72] proposed that the observed increase in plasticity could be the result of increasing dislocation density and/or their mobility. In this latter case, it was suggested that the increase in cation vacancies would increase the volume of the distorted zone neighbouring dislocations and thus enhance their mobility. Furthermore the presence of micropores in the scale would provide additional sources and sinks for dislocations.

As with wüstite, magnetite grows by outward movement of iron. Magnetite is also a metal deficit oxide ($\text{Fe}_{3-\delta}\text{O}_4$) in which both cation interstitial and cation vacancies may be present, and generally cation vacancies dominate at high $p(\text{O}_2)$ and interstitials at low $p(\text{O}_2)$ [109]. Magnetite has an inverse spinel structure in which the Fe^{2+} ions are all located at octahedral sites, but half the Fe^{3+} ions are located octahedrally and the other half tetrahedrally co-ordinated. Thus, there are two possibilities for vacant cation sites, but up to six for interstitial sites [123]. It is very difficult to define the detailed defect structure in terms of the site coordination. It is agreed that the minority defects in magnetite that control creep are most probably oxygen vacancies and Gomes et al. [124] have shown that these could be associated with iron vacancies. Dieckmann [109] concludes that since much of the work to measure oxygen diffusion was carried out in water-containing atmospheres, it is not possible to make unambiguous statements concerning the effect of water on transport in magnetite.

Haematite, $\text{Fe}_2\text{O}_{3-\varepsilon}$, forms by inward growth of oxygen, and the predominant defects are believed to be oxygen vacancies. The deviation from stoichiometry is small (about $\varepsilon = 10^{-5}$ at 1100°C) [125]. If water is incorporated in the oxide it would be expected to be as

protons resulting in formation of the OH^- ion. Dieckmann [109] modelled the dependence of the oxygen vacancy and OH^- concentration as a function of $p(\text{O}_2)$ and showed that the hydroxyl group concentration dependence, proportional to $p(\text{O}_2)^{-1/4}$, is much smaller than that of the oxygen vacancy. There appears to be no diffusion data for haematite in the presence of water vapour.

5.2.5. Nickel oxide

A helpful recent summary by Haugsrud [126] on the oxidation of nickel oxide details current understanding. The oxide is metal deficient with a relatively small non-stoichiometry, for example, the concentration of nickel vacancies at 1000 °C in 1 atm oxygen is about 10^{-3} – 10^{-4} (atomic fraction). The oxide grows predominantly by outward movement of cations, above about 1100 °C and bulk lattice transport is the dominant diffusion mechanism, but at lower temperatures grain boundary cation diffusion occurs. Frequently the oxide has a duplex-structure with a porous inner layer of small equiaxed grains and an outer layer of large columnar grains. This inner layer is believed to grow by inward migration of gaseous oxygen down grain boundaries and or micro-cracks in the oxide are formed due to build up of oxide growth stress. The more impure the nickel the greater is the extent of inner layer. Again, there is limited information on the effects of water vapour on transport properties, but as reported earlier, water vapour seems to have no effect on the oxidation of nickel.

5.3. Molecular diffusion

There are many reports in the literature of ingress of water molecules through oxides scales, and clearly for this to happen fissures need to be created, or as in the case of silica, an open network structure allows transport of large molecular species. The important consideration here, therefore, is the mechanism by which water vapour causes cracking of the scale, and this will be discussed in more detail in Section 6.

In addition, it is important to consider gaseous or volatile species that might be created during oxidation reactions involving water vapour, and how these are transported within the scale. The most well accepted process for vapour or gaseous transport not directly involving fissures is the dissociative mechanism first proposed by Rahmel and Tobolski [69]. It should be noted that this mechanism is only applicable for scales growing by cation transport and involves interaction with voids formed by vacancy condensation (see Section 3.2). It can be demonstrated that if a void contains both hydrogen and water vapour, oxidation of the surface nearest the metal will occur by reaction with water to form new oxide and the reaction product hydrogen, while a reduction reaction occurs at the surface of the void nearest the gas phase to produce water vapour. Thus it can be seen that this process provides for rapid inward diffusion of oxygen while the void gradually moves outwards from the metal/oxide interface to the oxide/gas interface. The process is schematically illustrated by Ehlers et al. [36] in Fig. 21.

Ehlers et al. [36] have recently proposed that one mechanism for pore generation in an Fe–9%Cr steel is by the reaction of water vapour with magnetite at low $p(\text{O}_2)$ near the scale alloy interface to form the volatile $\text{Fe}(\text{OH})_2$. The volatile hydroxide then diffuses through the scale to the outer surface where it is oxidised to Fe_2O_3 , as is schematically illustrated in Fig. 22. Using available thermodynamic data however, they calculate that the vapour pressure of $\text{Fe}(\text{OH})_2$ is too low to sustain the reaction, but point out that these

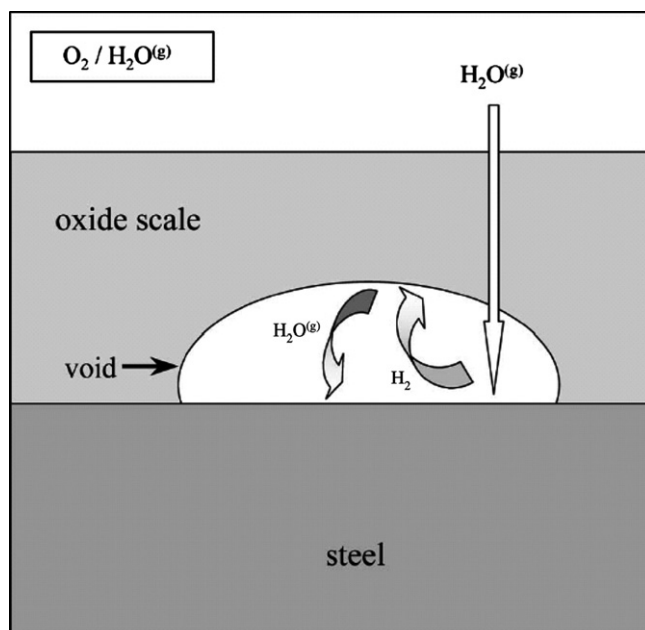


Fig. 21. Schematic illustration showing transport of water vapour molecules through the scale and oxygen transfer across in-scale voids based on the Rahmel Tobolski mechanism [69], after ref [36].

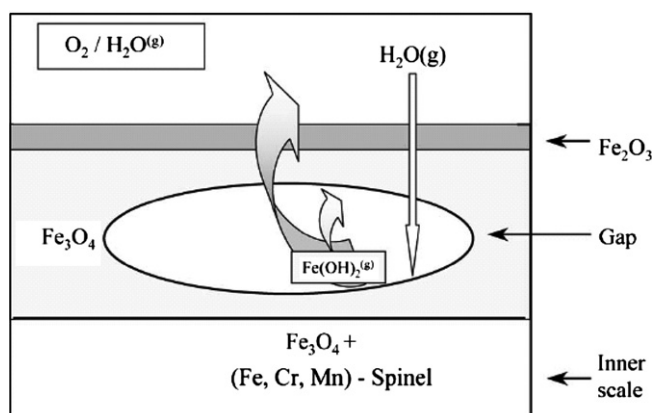


Fig. 22. Schematic illustration showing a proposed mechanism for void generation and transport of iron from the inner to the outer part of the scale formed on a Fe · 9%Cr steel in $N_2/1\%O_2/2\%$ water vapour at 650 °C, after Ref. [36].

data need verification. But the fact remains that vapour phase transfer occurred and $Fe(OH)_2$ is the only possible candidate. Furthermore Ehlers et al. have demonstrated that scales grown in water vapour mixtures are more permeable than those grown under dry conditions. This, they demonstrated by $^{18}O_2/H_2^{16}O$ studies as being the result of competitive adsorption between water and oxygen, with water being preferentially adsorbed if

the $p(\text{H}_2\text{O})/p(\text{O}_2)$ ratio is ≥ 1 . When scales are grown in water/oxygen gas mixtures under these conditions only water vapour participates in the reaction. It is proposed that the reaction of oxide with water vapour to produce $\text{Fe}(\text{OH})_2$ develops the porous structure in the magnetite scale. $\text{Fe}(\text{OH})_2$. It is of interest to note that Jacob et al. [18] reported that for chromium oxidised in $^{18}\text{O}_2/\text{H}_2^{16}\text{O}$ oxygen/water mixtures that oxygen derived from water was the major component of the oxide even though in that case the $p(\text{H}_2\text{O})/p(\text{O}_2)$ ratio was 0.05.

As has been demonstrated, void transport by the Rahmel and Tobolski or generation of volatile $\text{Fe}(\text{OH})_2$ require water vapour to exist within the oxide scale. In addition to proton diffusion, the presence of cracks and fissures in the oxide is another obvious mechanism to allow water ingress, and their origin will be discussed in the next section.

6. Mechanical effects

It has been noted that, particularly for the case of alumina, that adhesion of the scale is decreased when grown in the presence of water vapour [7–9], while for iron oxide based scales, adhesion was observed to improve [69,71,72] when grown in water vapour and this was believed to be the result of improved scale plasticity. An increased propensity for oxide cracking has been observed for chromia [31] and chromium-rich spinels that form on Fe Cr alloys [127]. Table 4 taken from the paper by Renusch and Schütze [127] clearly shows that the presence of water vapour causes increased acoustic emission (AE) that was associated with oxide cracking during cooling and oxide growth on a number of different chromium-rich spinels. No effect of water vapour in enhancing cracking of the two chromia-forming alloys (HK40 and Alloy 800H) was observed. For the spinel formers, however, AE emission occurred during oxide growth in wet gas mixtures thus clearly demonstrating that oxide growth stresses were modified by the presence of water vapour. It is possible, therefore, that water vapour either alters mechanical properties of some oxides, or as has been demonstrated the oxide growth process has been changed. Alternatively, at least for the cases where increased oxidation rates were caused by the presence of water vapour, the observed differences between wet and dry behaviour may simply be a function of the greater scale thickness.

A particular problem with steam oxidation of boiler tubes in power generation is that the oxide scale is prone to spall as it thickens, and the spalled oxide can then block the tubes themselves or be carried into the steam turbine and erode the blades [128,129]. There

Table 4
Qualitative acoustic emission results for some chromium-containing alloys oxidised in wet and dry conditions [127]

Materials	AE wet at high temperature	AE wet during cooling	AE dry at high temperature	AE dry during cooling
2.25%Cr 1%Mo	None	Yes with incubation	None	Yes
9%Cr (P91)	Yes	Yes	Some	Yes
9%Cr (Nf616)	Yes	Yes	None	Yes
12%Cr 1%Mo	Yes	Yes	None	Yes
Alloy 800H	None	Yes	None	Yes
HK 40	None	Yes	None	Yes

have been many attempts to model spallation but this requires an understanding of the stresses imposed on the oxide system and well as the mechanical properties of the scale.

The mechanical response of materials, in general, is very dependent upon the microstructure, and in cases involving fracture at an interface or within the material, the number and size of defects determines the behaviour. We have seen that when scales are grown in the presence of water vapour an increase in scale porosity is often observed. It would be expected therefore that through-scale cracking and lower adhesion would be characteristics of these scales. The following sections will briefly consider the sources of stress in an oxide layer and whether any stress relief processes operate. Mechanical property data for oxide scales grown in wet atmospheres will be considered and compared with corresponding data for dry oxidation. It will be demonstrated that such data are not very numerous, and generation of definitive data would be a fruitful topic for further work. In order to make use of the models now being developed it is important to acquire reliable data.

6.1. Stresses in oxide scales

Oxide scales can be stressed by a number of different mechanisms and these have been discussed in a detail in many papers and are well reviewed by Kofstad [71], Evans [130] and Schütze [131]. It is intended to give only a very brief account of the stress development in scales, so the reader should refer to the reviews cited above for more detail.

6.1.1. Stress generation

There are four main sources of stress in oxide scales. By far the most important contribution to oxide scale stress comes from thermal effects, σ_{th} , during thermal cycling due to the generally large differences in thermal expansion coefficients between the metal and oxide, and this usually results in compressive stress in the oxide when cooled to ambient temperatures; one important exception is the case for Fe–Cr steels where multilayered scales develop and tensile stresses develop (see later discussion).

Growth stress, σ_{gro} , is a consequence of differences in molar volume between the metal and the oxide, and usually the oxide volume is the larger; the ratio oxide volume/metal volume is known as the Pilling Bedworth ratio. Ratios greater than one result in the oxide scale being in compression when oxide growth occurs at the metal/oxide interface. Growth may also occur at the oxide/gas interface (in which case it may appear to be unconstrained and no stress would be expected) but it must be borne in mind that if the oxide is to remain adherent then it must recede with the metal and thus again be subjected to compressive stress. Where both anion and cation diffusion take place then growth will occur within the scale. Thus it is not always possible to determine the growth stress from simply applying the Pilling Bedworth concept.

In the case of engineering alloys compressive stresses are the norm, although during the transient stages of oxidation where phase changes occur this can give rise to transformation stresses, σ_{trans} . For example, tensile stresses may be generated during the formation of α -alumina at high temperature ($>$ about 1000 °C) due to the transformation from θ -alumina which is stable at intermediate temperatures with a resultant 9.7% reduction in molar volume [132,133]. Or for the iron-base system, transformation of magnetite to haematite can occur when voids develop in the scale resulting in a net compressive stress of about 10% when oxygen is the mobile species [83,134]. Tensile stress in the external scale may

also arise from oxygen solution in the alloy or from internal oxidation and when the material is heated above the oxide formation temperature.

Curvature of the substrate material will also contribute to total stress in the system, σ_{geo} . Depending on whether the oxide growth is predominantly by cation diffusion (new oxide at outer surface) or anion diffusion and whether the surface is convex or concave, either tensile or compressive stresses will result. For example, for a concave surface and cation diffusion oxide growth at the outer surface will be constrained to a smaller volume than that which would have formed on a flat surface and thus cause compressive stress.

Finally, any system applied stress, σ_{app} , must be considered. The total stress, σ_{tot} , in the oxide scale will be the sum of these individual effects as shown below:

$$\sigma_{\text{tot}} = \sigma_{\text{th}} + \sigma_{\text{gro}} + \sigma_{\text{trans}} + \sigma_{\text{geo}} + \sigma_{\text{app}} \quad (14)$$

There are only a few examples of growth stress measurements on oxides formed in moist atmospheres, and one such is the work of Schütze et al. [135,136] where it was demonstrated that the growth stress of scales formed on 9% Cr steels (Nf616, E911 and P91) at 650 °C in air + 10% water was about 5 times that for the same materials when oxidised in dry air; compressive stresses were observed in both wet and dry conditions. Under dry conditions the scale on E911 was chromia, but when oxidised in wet air, the initially formed scale is a chrome-rich spinel. The difference in oxide phase that formed in the two conditions would only change the growth stress by 27% based on differences in Young's modulus, so that it is clear that the presence of moisture significantly increased the growth stress. It was proposed that formation of the volatile $\text{CrO}_2(\text{OH})_2$ depleted the surface sufficiently so that chromia could not form when tests were carried out in wet air.

Garcia Vargas et al. [137] used *in situ* X-ray diffraction to monitor the growth of scales formed in air and air + 10% water vapour at 800 °C on Nicrofer 45TM and F17TNb, Ni-base and Fe-base alloys, respectively, being considered as potential candidates for SOFC interconnects. They observed variable intensity of the chromia lines when grown in the moist atmosphere which they interpreted as being the result of spallation at temperature due to increased growth stress. Particularly with Nicrofer 45TM, the effect of water vapour was to encourage formation of silica at the alloy/scale interface which was a consequence of water vapour promoting inward migration of oxidant.

6.1.2. Stress relief

It has been demonstrated that stress relief processes can occur by creep of the substrate or oxide and/or by cracking of the oxide. Whether the oxide or substrate is the dominant process will clearly be decided by the relative creep rates, and generally metallic materials have a high creep rate than oxides with the notable exception of some iron oxides [138]. In considering creep deformation of the oxide it is important to distinguish between dislocation and diffusion creep, where the latter only occurs at homologous temperatures in excess 0.7 of the melting point. Generally, temperatures are too low for diffusion creep to occur in the oxide when alumina and chromia scales are formed, but for vitreous silica creep (viscous flow) has been observed. Iron oxides have relatively low homologous temperatures and thus diffusion creep is possible at temperatures in excess of 900 °C (see Table 5). Dislocation creep is considered in some systems particularly iron oxides where homologous temperatures are relatively low. Creep relaxation is only active while the material is still at high temperature and the oxide is growing, so that in most cases

Table 5

Homologous temperatures of some common oxides and metallic materials

	Melting point (°C)	Melting point (K)	$0.4T_m$ (K)	$0.4T_m$ (°C)	$0.7T_m$ (K)	$0.7T_m$ (°C)
FeO	1370.0	1643.2	657.3	384.1	1150.2	877.1
Fe ₂ O ₃	1565.0	1838.2	735.3	462.1	1286.7	1013.6
Fe ₃ O ₄	1594.0	1867.2	746.9	473.7	1307.0	1033.9
NiO	1960.0	2233.2	893.3	620.1	1563.2	1290.1
Cr ₂ O ₃	2450.0	2723.2	1089.3	816.1	1906.2	1633.1
Al ₂ O ₃	2054.0	2327.2	930.9	657.7	1629.0	1355.9
SiO ₂	1710.0	1983.2	793.3	520.1	1388.2	1115.1
Fe	1535.0	1808.2	723.3	450.1	1265.7	992.6
310	1420.0	1693.2	677.3	404.1	1185.2	912.1
Ni	1455.0	1728.2	691.3	418.1	1209.7	936.6
Nim 75	1360.0	1633.2	653.3	380.1	1143.2	870.1

when the oxidation temperature is greater than about 700 °C and for long-term oxidation all stresses other than those resulting from thermal transients will be reduced and often to negligibly small values. Where oxide cracking is the stress relaxation process, through-thickness scale cracking would result in direct access of the oxidant to the substrate and thus acceleration in the oxidation rate would occur.

In contrast to the above, under thermal cycling conditions, the stress relaxation produced during cooling can have a deleterious effect on oxide integrity. Such relaxation produces a “creep hysteresis” loop and results in the development of in-plane tensile stresses on the return to high temperature. Finite element calculations indicate that these stresses can be sufficiently large to produce through-thickness cracking of the oxide layer after only a single cycle to intermediate temperatures. In this case, insertion of a hold period at lower temperatures increases the tensile stress subsequently developed. The predictions have been validated experimentally for a chromia-forming austenitic steel [139] and an alumina-forming alloy [140,141].

6.2. Scale mechanical properties

The mechanical properties of many of the scales of interest to this review are quite well established when formed in “dry” conditions. The topic was reviewed in 1994 at a conference at National Physical Laboratory [142]. However, data on the properties of oxide scales formed in moist atmospheres is sparse. Although it must be remembered that much of the existing data was obtained in ambient air and thus may be to some extent affected by the presence of moisture. There is a clear need to make measurements under dry conditions to determine whether the presence of 2–3% water vapour has a significant effect on the mechanical response of oxide scales. It has frequently been proposed [143] that crack propagation in ceramics can be assisted by the presence of water vapour so that some of the data on the fracture behaviour in ambient laboratory conditions may be low. For example, early work by Grosskreutz [144] showed that the fracture strength of alumina was increased by about 1.5 times when measured in vacuum compared with air. Moisture assisted cracking of silica was observed by McElhaney and Ma [145] due to penetration of cracks by moisture, and then the subsequent expansion of the lattice due to incorporation of water increased stress at the crack tip resulting in faster crack growth.

Otsuka [146] conducted room temperature tensile three point bent-beam tests on preoxidized specimens of ferritic 2%Cr (T22), 9%Cr (T91), and 12%Cr (T122) steels oxidized in steam between 550 and 750 °C in order to examine the fracture and spalling behaviour of steam-grown oxide scale. For the 2%Cr steel, local scale exfoliation resulted for preoxidized specimens where the scale thickness was 380 µm or greater. For a thickness of 75 µm or less, the scale was intact and no macro-cracks were observed, but fracture occurred at a tensile strain of 0.2–0.3%. The fracture mode was through scale cracking accompanied by scale detachment. For oxide scales formed on the 9%Cr and the 12%Cr steels, macro cracking and exfoliation were not observed on the preoxidized specimens. Through-scale cracking resulted upon applying a tensile strain of 1.86%, the oxide scale remained adherent and there was no exfoliation. Spalling resistance of the scale formed on the 9%Cr and the 12%Cr steels was much greater than the scale formed on the 2%Cr steel. Since the three-point bent-beam test was conducted at room temperature, thermal strains arising from different linear expansion coefficients between the oxide scale and the base metal upon cooling must also be considered, and when this is done the fracture strain for the oxide scale on 2%Cr steel was the sum of the cooling strain of 0.1% [83] and the critical fracture strain of 0.2–0.3% obtained by Otsuka [146]; i.e., 0.3–0.4%. It should be noted that for steam plant, where oxide forms on concave surfaces, this additional constraint will add a compressive component to the calculation of the total stress.

For comparison with scales formed under “dry” conditions, Nagl et al. [147] observed that with mild steel oxidised at 550 °C in ambient air containing about 2% water vapour the measured failure strains at oxide growth temperature increased slightly (about 0.05%) when the strain rate was reduced from $\sim 10^{-4}$ to 10^{-5} s^{-1} . This behaviour was explained by limited oxide creep in the short time scale during deformation up to oxide failure and it is expected that the strain increment due to creep would further increase with lower deformation rates. A similar difference was found for the failure strains measured at room temperature for scale formed at 550 °C. In this case the compressive cooling stresses of approximately 0.05% must be overcome before the oxide experienced tensile stresses. The cooling strains agreed well with X-ray strain measurements and calculations based on the thermal expansion coefficients of oxide and substrate. In all cases, measured failure strains decreased with increasing oxide thickness. However, the data showed considerable scatter that was reduced significantly when the data were plotted directly as a function of composite void size which was determined by examination of polished cross sections; tensile fracture strain varied between 0.1% and 0.5% depending on scale thickness. Berchtold et al. [148] investigated the high temperature deformation of iron oxide scales grown on 1% Cr 0.5% Mo steel at 500 °C in air using strain rates between 2.8×10^{-9} and $1.5 \times 10^{-6} \text{ s}^{-1}$. The specimens were heated by an electric current and cracking could be observed *in situ* using a microscope with a long focal length. With deformation rates, $\gtrsim 10^{-8} \text{ s}^{-1}$ no cracks were detected, even for strains of 2% and this behaviour was mainly attributed to oxide creep even at these low temperatures.

It would appear therefore, that steam grown scales on iron-base alloys were more strain tolerant at room temperature than those formed under dry conditions. As has been demonstrated by Schütze et al. [135,136] cracking of scales formed on these materials was observed during oxidation in atmospheres containing moisture, and it is possible therefore that the enhanced fracture resistance could be attributed to the presence of such cracks, thus giving rise to an apparent increase in deformation resistance. The absence of cracking in high temperature tensile tests at low strain rates in air with ambient moisture levels

indicates that creep relaxation is occurring [148]. Unfortunately it is not clear that this is an effect of moisture since no tests were carried out under completely dry conditions.

6.3. Spallation–adhesion

Dieckmann [109] in his review of the effect of water on transport processes also briefly considers adhesion. He points out that with Pd alloys containing internal oxide particles, any hydrogen introduced into the system preferentially segregates to the metal oxide interface [149,150] and suggests that hydrogen may act similarly when present in the systems considered in this review and thereby weaken the metal/oxide interface. On this point the evidence is somewhat contradictory. For the chromia-forming alloys hydrogen is known to be present, but there is little evidence that scale adhesion is in anyway degraded, if fact the opposite seems to be true for the case of chromium metal oxidation [18–21]. With iron chromium alloys water vapour induces breakaway oxidation and here it is proposed that the initially formed protective chromia layer fails as a result of scale cracking [23,31], and this may be attributable to the effects of hydrogen or hydroxyl ions. Also, for alumina-forming alloys a common observation has been that the presence of water vapour encouraged spallation [7–9] particularly if the scale was prone to cracking when formed in dry atmospheres. For the iron–chromium system where breakaway oxidation occurs the resulting scale microstructure contains many voids [36,31] and spallation is common. Dieckmann [109] also refers to some *ab initio* calculations for the Cu/SiO₂ system that show that OH terminated silica is a weaker bond than OO terminated silica [151,152] thus supporting the suggestion that adhesion may be reduced when hydrogen, or hydrogen-containing species, segregates at interfaces. Dieckmann [109] further suggests that segregation of hydrogen containing species may also be favoured when the interfaces are under tensile stress, and thus again encourage spallation.

There appears to be very little data on the adhesion of scales formed in moisture containing atmospheres. Some qualitative information was reported by Hou and Saunders [153] on failure of steam grown scales on 9% Cr steels. In this case, in pull and indentation tests on 9% Cr steels cohesive failure was observed and failure occurred at the spinel/magnetite interface or within the magnetite layer where pre-existing voids were evident.

Thus while it is frequently sometimes reported that scale adhesion is reduced in moist atmospheres, there seems very little definitive data to support these observations. It is possible that many of the reported observations are a consequence of either changes in oxide growth mechanism or in the oxidation rate, rather than in the property of the scale *per se*. Perhaps one clear example where the interfacial adhesion is altered is for the case of alumina-forming alloys, where generally water has no significant effects on growth rate or microstructure, but scales that normally crack under dry conditions are more susceptible to spalling when in moist environments. Evidently moisture ingress through the cracked scale alters bonding at the interface as proposed by Dieckmann [109].

6.4. Modelling

Modelling of spallation has been a major activity in high temperature oxidation and significant process has been made. These models find general applicability and thus with the correct input data should be capable of predicting behaviour of oxide scales grown in the presence of water vapour. However, as the forgoing discussion has indicated the

input data required for these models is very limited in the case of moisture containing environments so that at present the use of existing models to predict the spallation of scales formed in will be somewhat questionable. However, it should be noted that one of the early models developed for the Electric Power Research Institute (EPRI) in 1978 was for steam grown oxides formed on boiler steels used in power plant [83]. In that case, the mechanical property data used was largely based on air formed scales, and use was made of the Critical Strain Energy Criterion (CSEC) for spallation first developed by U.R. Evans in 1948 [154]. The basis of this so-called EPRI model is outlined below:

Fractures in tension occur at a certain strain by the extension through the scale of cracks originating from the surface defects in the layer. When the flaw size is small compared with the oxide thickness the fracture equation for propagation of a crack in simple tension is:

$$K_{1c} = 1.12E\varepsilon_c\sqrt{\pi c} \quad \text{and with} \quad K_{1c}^2/E = 2\gamma \quad (15)$$

$$\text{this gives } 2\gamma = 1.12^2 E \varepsilon_c^2 \pi c \quad (16)$$

where K_{1c} is the critical stress intensity, γ is the fracture surface energy density, E is the elastic modulus, ε_c is the critical strain and c is the depth of the initiating crack.

A more general formulation of this failure criterion where the flaw size in the oxide scale was taken as being equal to the scale thickness (which is a permissible conservative approach to scale failure) led to the following energy related description [83], i.e. failure occurs when

$$\frac{\text{stored energy per unit interfacial area}}{\text{shear fracture surface energy per unit interfacial area}} > 1 \quad (17)$$

The stored energy per unit area in a single phase layer assuming elastic deformation is given by:

$$\frac{hE\varepsilon|\varepsilon|}{2(1-\nu)} \quad (18)$$

where, h is the scale thickness and ν is the Poisson's ratio, and $\varepsilon|\varepsilon|$ is used rather than ε^2 to distinguish between tension and compression.

Thus the criterion for spalling becomes:

$$\frac{hE\varepsilon|\varepsilon|}{\gamma'} > 1 \quad (19)$$

where γ' is a parameter proportional to the shear interfacial surface fracture energy density, γ , but incorporates Poisson's ratio, numerical factors and an additional factor, I , to account for the increased difficulty of initiation compared with subsequent propagation of a delaminating crack.

$$\gamma' = 4(1-\nu)I\gamma \quad (20)$$

Based on Eqs. (17)–(19) a general diagram was developed showing failure modes as a function of oxide thickness and imposed strain [83] that is shown in Fig. 23.

While this model has been of value it is now recognised that improvements are needed, and EPRI is actively promoting its further development. At recent conference all aspects of steam oxidation were reviewed including modelling, and three contributions

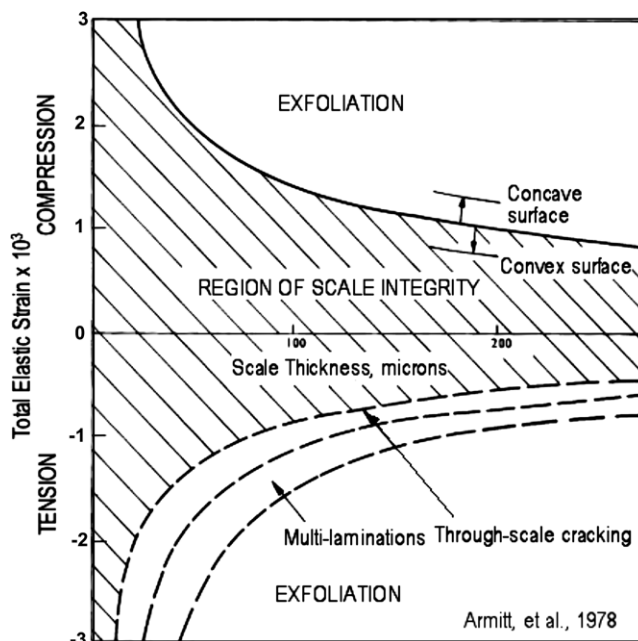


Fig. 23. Oxide failure modes as a function of oxide thickness and imposed strain, after Ref. [83].

on modelling spallation are summarised below. Three different approaches were taken, one in which tensile failure initiated spallation, the other where the principal failure mode was compressive, and the final paper considered the total model.

The ultimate design objective is to be able to use models to predict the formation of the various oxide layers during oxidation, and the onset of damage in the form of through-thickness tensile scale cracking and the subsequent layer debonding that leads to time-dependent spallation and an increase in unwanted debris within power plant systems. One very important precursor to spallation is the formation of through-thickness scale cracks that can be induced by thermal stresses alone or by combinations of thermal and growth stresses and applied loads that are inevitable in pressurised power plant. Two engineering approaches to predicting scale cracking can be made leading to two differing consequences. Firstly, scale cracking can be considered to occur when the tensile strain in an oxide layer reaches the critical failure strain of the layer that is the material property controlling scale failure. A consequence of this assumption is that an oxide layer of any thickness will always fail at the same strain, and this is not observed in practice. It is well known that thicker oxide layers will crack at a lower strain than thinner layers. One explanation of this phenomenon is the presence of crack-like defects within the oxide scale, as described in the EPRI Report [83], where a major problem is knowing the critical defect size that should be used with energy-based fracture mechanics concepts. In [83] no account was taken of the fact that the thermo-mechanical properties of the oxides scales differ from those of the steel substrate, nor of the fact that property differences between layers lead to the presence of significant thermal stresses. These problems can, however, be overcome by considering a steady-state through thickness cracking model [McCartney in 159] that has

been developed from models that predict ply cracking in composite laminates subject to thermal stresses and general in-plane loading. A software system known as PREDICT [156] has been developed to enable such predictions to be made. Such software can easily be applied to the prediction of through-thickness cracking in oxide scales, as shown by results presented by McCartney [155]. The steady-state cracking model assumes that a long through-thickness crack exists within a given oxide layer, and considers the applied loading and temperature conditions for which it is energetically favourable for the crack to grow within that layer. The effective fracture energy for through-thickness cracking replaces the critical strain to failure as the parameter that controls cracking. This approach will lead to lower bound predictions of the cracking stress that enable conservative estimates to be made. Additionally, the approach leads to the consequence that the cracking stress (or strain) depends on the properties and thickness of the cracked layer, and of the other layers, as well as the fracture energy. The other very important precursor to spallation of oxide layers is the development of debonded interfaces between one or more of the oxide layers, although cavitation and cavity coalescence at interfaces may also be an additional important mechanism but that has yet to be modelled.

In considering compressive failure in scales, Evans [138] proposed that CSEC approach does not attempt to account for growth of the interface crack, nor of the stress intensification that must exist at the locations in the interface where through-thickness cracking has occurred, but it does lead to an analytical formula that enables useful predictions for the temperature drop required to cause spallation. For compressive stresses within the oxide scale, Evans [138] described and analysed the phenomenon of wedge cracking that occurs when through-thickness cracking, which initiates interfacial debonding, is at an angle of about 45° to the interface between the layers.

An important but largely unanswered question posed by Evans [138] is whether the CSEC can be used reliably to predict oxide spallation from alloys exposed at lower temperatures. Mechanistic understanding has now improved to the extent that it is known that the CSEC can apply to an interfacial wedge cracking process but only if creep relaxation can occur sufficiently rapidly during cooling that crack growth takes place over a narrow range of temperature. Finite element modelling of wedge cracking of a chromia layer has shown that creep is sufficiently fast in Type 316 steel for this to occur during cooling from 600 °C. The situation is less clear, however, for the spallation of multilayered iron-rich oxides grown on ferritic steels although there is experimental evidence for wedge cracking at both oxide/oxide and oxide/substrate interfaces. Creep relaxation in this system is most likely to occur within the magnetite layer but detailed computations of the crack growth kinetics, supplemented by experimental studies of oxide spallation, are needed in order to validate the CSEC as a predictive method for this system. Implicit in this is the need to characterize the dominant cracking process and, in particular, the rôle played by through-layer tensile cracking. It is also clear that there is uncertainty over the stress state within the respective oxide layers of the scale grown on ferritic alloys both at the oxidation temperature (growth stresses) and during cooling (thermal stresses). It is known that, in high temperature alumina-forming alloys, growth stresses can be initially high but may be relaxed by creep deformation of the substrate alloy. Relaxation rates will be much reduced at typical operating temperatures for ferritic alloys and it is feasible that large growth stresses could develop. They may have added significance in these systems where thermal stresses tend to be relatively low because of the small differences between the thermal expansion coefficients of the respective components.

Schütze [157,158] has discussed the many factors that contribute to the conditions for through-thickness scale cracking and spallation. The major thrust of his approach is to recognise that ideally all these factors will need to be incorporated into a predictive methodology that enables the conditions for spallation to be determined in an engineering context. One aspect of the approach is to use the ‘EPRI diagram’ (Fig. 23), defining regions in ‘elastic strain-scale thickness’ space for scale integrity, through-scale cracking, multi-laminations and spallation, as a user-interface between engineers and the predictive models that can be used to assess the various failure mechanisms with respect to oxide system and its geometry. Such a user-interface, if it is to be useful and reliable, must be based on the best available model for each mechanism considered.

Recently [159] the EPRI diagram has been modified to allow the scale thickness in the original EPRI diagram to be replaced by a parameter (ω) that incorporates all of the various oxide property related parameters, and which essentially is the criterion for scale failure. Stored strain energy in the scale or accumulated strain (ε) is retained as the other main parameter, but the models and equations needed to calculate this, as well as the new oxide scale property parameter, are included in the background behind the classic EPRI approach. Fig. 24 illustrates the next generation EPRI diagram that can be developed. The diagram envisages various levels of input data.

The different levels (1, 2, 3...) indicated in Fig. 24 contain increasing detail. As an example, for calculating the accumulated strain (ε) in the oxide:

Level 1: will represent the residual elastic strain from plant operation, which will be the sum of the strains imposed by growth of the oxide ($\varepsilon_{\text{grow,int}}$); by geometric factors that affect the oxide growth ($\varepsilon_{\text{grow,geo}}$); the stresses from thermal excursions ($\varepsilon_{\text{therm}}$); and strains from external loading (ε_{ext}); minus the strain relief due to creep of the oxide and/or alloy ($\varepsilon_{\text{creep}}$); and from other forms of deformation such as pseudo plasticity ($\varepsilon_{\text{pseudo-pl}}$). That is: $\varepsilon = (\varepsilon_{\text{grow,int}} + \varepsilon_{\text{grow,geo}} + \varepsilon_{\text{therm}} + \varepsilon_{\text{ext}}) - (\varepsilon_{\text{creep}} + \varepsilon_{\text{pseudo-pl}})$.

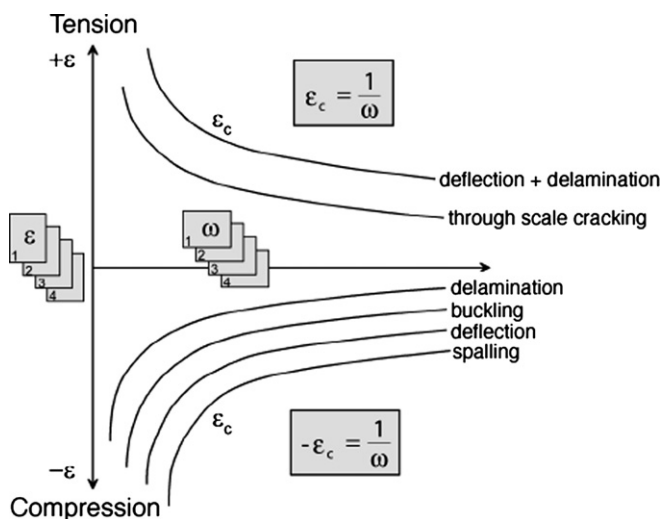


Fig. 24. The next generation EPRI diagram, after [159].

- Level 2: will include models that will allow the calculation of strain from each of these causes;
- Level 3: will incorporate models that calculate specific parameters used in the Level 2 models; these will include, for instance, the temperature dependence of particular parameters. This level, or further sublevels will accept plant data as input.

For the scale property parameter (ω):

- Level 1: will represent a critical strain for scale failure (ϵ_{crit}), where $\epsilon_{\text{crit}} = 1/\omega$.
- Level 2: will address the modes of scale cracking.
- Level 3: will incorporate other models as needed. For instance, there is a need for improved models to describe the details of oxide scale failure, including delamination, cracking, and local spalling.
- Level 4: will contain models for calculating the parameters required, including: oxide thickness; the elastic modulus and fracture toughness of the scale; surface energies; pore sizes; and geometric parameters. These are related to plant data through algorithms.

For this diagram to be of use to engineers and scientists it is essential that various models be validated, and possibly a combination of different aspects of those proposed above [155,138,157] is needed, as well the generation of relevant data for the systems of interest. The obvious complexity of such an approach is, however, considered acceptable given the current power of modern computers. In conclusion, it should be stressed that while this approach has been developed for the case of steam oxidation in power generation boilers, it has general applicability for oxide scale spallation in all environments, provided the input data is available. Obtaining this data will be a major challenge for materials scientists of the future.

7. Concluding summary

Energy generation in all its forms including electrical power, automotive and aeronautical motive power relies upon combustion of different fuels (fossil and bio-fuels and with the advent of the hydrogen), and upon combustion all these fuels produce water vapour in varying amounts. Furthermore, steam generation is an essential part of power generation and in heat recovery systems that are used extensively in process industries. Thus it is clear there is a large industrial base that is dependent upon reliable operation of materials exposed to water vapour at high temperature.

The presence of water vapour in gas mixtures causes the rate of oxidation of most metals, and alloys and non-oxide ceramics to increase, with materials forming alumina and nickel oxide being two notable exceptions. The largest effect of water vapour is found with the iron chromium system, where in dry atmospheres a protective scale usually forms, but breakaway oxidation results for alloys with up to about 15% Cr with oxidation rates increasing by at least an order of magnitude, although once breakaway has occurred rates generally decrease. Likewise, dilute FeAl and FeSi alloys show similar behaviour. The oxidation rate of pure chromium metal is also increased but in this case the increases observed are usually less than about a factor of two. The Ni.Cr system is somewhat anomalous, with variable results being reported, some workers reporting little effect and others

showing a small effect. Rates of attack on iron are only increased when exposed at temperatures above about 900 °C and the presence of trace impurities can have a significant effect. Silica is also considered in this review because of its importance in the microelectronics industry, but also because for very high temperature protection silica is often considered as a protective oxide. In this case also the effect of water vapour is to increase rates of oxidation. It should be noted that these general results have been obtained from a wide range of gas mixtures containing water vapour. Nitrogen and argon have been used as carrier gases, as well as mixtures containing other oxidants such as air, oxygen and carbon dioxide, and hydrogen water mixtures and pure steam. As reported the effects of these other gases on oxidation in the presence of water vapour can be very influential.

The first question that has been addressed is why water causes this increase in reaction rate. In any solid/gas reaction, a first essential step is adsorption and, when subsequent reaction product growth is by ionic transport, dissociation of the reactant gas. In the case of water either partial dissociation to OH^- and H^+ or complete dissociation into oxygen and hydrogen is possible. Examination of the surface science literature indicated that water adsorption and dissociation is favoured on surfaces containing defects, and in addition acidic materials are the preferred reactants. The acid/base nature of surfaces can be described on a macro and micro scale leading to somewhat contradictory conclusions. For example, the Al^{3+} ion is a hard acid and reacts strongly with water but the alumina surface as a whole is basic when considering the PZC. The latter seems to control the reaction with water, since, as just mentioned, water has little effect on the alumina-forming alloys. The highly stoichiometric nature of alumina would further inhibit reaction. Furthermore, in general, water is the preferred reactant in gas mixtures. Where isotopic labelling has been used, frequently the source of the oxidant has been shown to be water even when present as a minor constituent of the gas mixture. The acidity of thermally grown oxides needs to be established so that the concept of acid–base reactions can be better understood. In the case of titania it was shown that the PZC of thermally grown oxides is the same as that of a powder when measured at room temperature. Further work is required to verify this on other oxide systems, and importantly to establish the effect of temperature on the acid/base nature of the surface.

When present in a mixture of gases, competitive adsorption is possible, and the evidence currently available suggests that water is usually the preferred adsorbent. Again, much of the work relating to this topic comes from observations at room temperature, but some high temperature data supports this general finding. There is a suggestion that water adsorption on the surface of growing oxide particles acts to form a more permeable scale and thus allow gas access and thereby enhances the reaction rate. Furthermore, oxygen dissociation may be the favoured reaction at high temperatures.

After adsorption and dissociation reactions, oxidation, or transport of oxidant must be considered. If oxidation rates are to be increased it is clear that transport of oxidant must also be increased. Two main mechanisms have been identified. Firstly, by molecular diffusion through cracks and pores, and secondly by lattice transport, and for the latter an increase in the lattice defect concentration is required. The dissociation products of water vapour are believed to be incorporated into the oxide lattice as protons or hydroxyls. The literature demonstrates that hydrogen dissolves as protons and is bound to oxide ions to form the substitutional hydroxide $(\text{OH})_{\text{O}}^\bullet$. These defects may equivalently and more simply be described as interstitial protons, $\text{H}_i^\bullet$. When combined as a hydroxyl, fast transport via the Grotthuss proton hopping mechanism promotes inward migration of “water”, but

simultaneously to maintain charge neutrality, there is an increase in cation vacancy concentration so that where oxide growth is by cation movement growth rates are increased both as a consequence of increased flux of anions and cations. Another frequent observation is that oxide plasticity/adhesion is improved when the oxide was formed in moist environments compared with that formed under dry conditions, and this is believed to be the result of the increased inward flux of oxidant.

The increase in cation diffusion rates can lead to the formation of pores within the scale at the metal/oxide interface by a vacancy condensation process. The presence of these pores gives rise to a further mechanism for oxide growth for scales formed in moist atmospheres. It can be demonstrated that if water can penetrate into the pore, oxidation of the surface nearest the metal will occur by reaction with water to form new oxide and the reaction product hydrogen, while at the surface of the pore nearest the gas phase the oxide is reduced by hydrogen to produce water vapour, with the net result that the pore moves outwards through the scale. This dissociation reaction, therefore, enables rapid transfer of oxidant through the scale. In the absence of such a mechanism to transport materials across the pore, the presence of pores would be expected to reduce the oxidation rate by interrupting the diffusion path of the reactants. The water vapour within the pore could be generated by proton hopping, or by the presence of micro-cracks allowing access of molecular water.

An important effect of the presence of water vapour is that volatile hydroxyl compounds can be formed. Considering the volatility of the three main protective oxides, alumina, chromia and silica, volatility increases in the order alumina < silica < chromia as $\text{Al}(\text{OH})_3$, $\text{Si}(\text{OH})_4$ and $\text{CrO}_2(\text{OH})_2$, respectively. In low $p(\text{O}_2)$ atmospheres, such as pure steam the volatility of $\text{CrO}_2(\text{OH})_2$ is reduced and, thus, is not a significant factor in oxidation reactions in these atmospheres; a similar effect is not expected for silicon and aluminium hydroxides, since their formation does not involve reaction with oxygen. There are a number of examples in the literature where loss of chromium and silicon from the scale due to volatilization has resulted in reduced protection of chromia- and silica-forming materials.

Other volatile reaction products of significance are tungsten, molybdenum and iron hydroxides; in the case of $\text{Fe}(\text{OH})_2$, however significant volatility is only important in low $p(\text{O}_2)$ atmospheres. One suggestion for the origin of porosity in iron and iron-based alloys is the formation of $\text{Fe}(\text{OH})_2$ within the scale assuming that water vapour can penetrate the scale by migration through micro-cracks for example. The volatile hydroxide so produced would escape to the outer, higher $p(\text{O}_2)$, region of the scale and react to form oxide and water, so that an “active” oxidation process, such as is found in chlorine-containing gases, could ensue.

In some cases scales formed in water vapour are prone to crack formation and eventual spallation, while others show greater plasticity and improved adhesion than when formed under dry conditions. It has therefore been important to consider the mechanical properties of scales and whether growth processes are altered such that there are changes in the stress state of the scale. There is limited data on the mechanical properties of scales formed in moist environments, although existing data for scales in “dry” conditions may be somewhat flawed due to the fact that most measurements were made under ambient laboratory conditions. Nevertheless, it is most likely that observed changes in the mechanical behaviour of scales formed in moist atmospheres is the result of alterations to growth processes. The increased oxidation rate of scales formed predominantly by cation transport, chromia and magnetite for example, would lead to a counter current of vacancies and likely void formation at the scale alloy interface. The presence of these voids in the scale promotes

fracture and eventual spallation. It has also been demonstrated that increased inward migration of oxidant occurs and, as with the rare earth effect, improvements in scale adhesion result. For the case of alumina scales, while water vapour generally had no effect on oxidation rates, adhesion was often adversely affected. In this case it is proposed that if the scale was cracked, as a consequence of thermal stresses for example, then penetration of water to the alloy/scale interface would result in weakened bonds and thus lower adhesion.

The observation of acoustic activity and of increased growth stress during the formation of scales formed on Fe 9% Cr steels in moist atmospheres is interesting. The acoustic signal provides good evidence that oxide scale cracking is occurring during oxide growth so that the presence of micro-cracks frequently proposed by other workers finds some justification. Thus, it would appear that direct access of water vapour to pores and voids can indeed take place, and thereby provide a mechanism for the dissociative transport across voids and formation of the volatile iron hydroxide. It can be argued, of course, that if cracks exist, then these of themselves are sufficient to account for the observed inward transport of oxidant and the dissociative mechanism need not be invoked. It is possible therefore that crack closure, due to re-oxidation may also be occurring.

The final section of this review considered spallation models. It was shown that a good understanding of the requirements for improved models has been developed and implementation is feasible using modern computers. The models that have been proposed however are complex and require a major effort to furnish the required data.

8. Recommendations

The following list, which is certainly not complete, suggests some research activities that could be profitably carried out in order to improve our understanding of the effects of water vapour on high temperature oxidation:

- Determine the acid–base nature (ABN) of thermally grown oxides.
- Investigate the effect of temperature on ABN.
- Determine adsorption and dissociation of individual gases on metal and oxide surfaces in gas mixtures at high temperature and define selectivity and reaction rates where competition could occur.
- Measure oxide scale gas permeabilities.
- Clarify the effect of water vapour on nickel-based alloys.
- Explore doping of oxides to mitigate the effects of water vapour.
- Conduct further work with *in situ* acoustic emission to determine the extent of oxide cracking at growth temperature and during cooling.
- Measure growth stress of oxides scales formed in moist atmospheres.
- Use the sulphur decoration technique to determine whether crack closure occurs during oxidation.
- Develop database on relevant mechanical properties of oxide scales to facilitate modelling.

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