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High-temperature chlorine corrosion of metals and alloys

A review

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High-temperature (> 200°C) corrosion of metals and alloys in atmospheres containing Cl_2 and/or HCl, which are widely encountered in many industrial environments, is reviewed. Topics include high-temperature corrosion mechanism and kinetics, thermodynamic considerations, and effects of gaseous components in the atmosphere (oxygen, air, water vapour, sulphur dioxide, and nitrogen) on the corrosion.

1. Introduction

Chlorine and hydrogen chloride gases either as reactants, products, by-products or as contaminants are widely encountered in chemical and metallurgical industries such as coal-fired boilers [1], waste incinerators [2, 3], plastic/polymer decomposition mills [4], vinyl chloride monomer mills [5–9], and recuperators [10]. For example, regardless of the molecular structure of the chloride-containing compounds in the fuel, at the flame temperature it becomes molecular Cl_2. Furthermore, during cooling, Cl_2 may also be converted to HCl by reacting with either hydrogen or water vapour. Table I is a list of these environments summarized by Elliott *et al.* [11]. Structural materials in such environments often corrode at accelerated rates at high temperatures because the corrosion products consist of chlorides which generally have lower melting points and boiling points than the oxides of the same metals [12]. In 1976, a review paper on halogen corrosion of metals was published [12] with emphasis on the thermodynamics properties. Since then fundamental studies have complemented work on metals and alloys. Recently, another review on corrosion in chlorine environments was published [13] with emphasis on performance of various materials as well as on materials limitations in such environments. The present paper discusses the high-temperature corrosion of metals and alloys in atmospheres containing Cl_2 and/or HCl. Topics include high-temperature corrosion mechanism and kinetics, thermodynamic considerations, and effects of gaseous components in the atmosphere (oxygen, air, water vapour, sulphur dioxide, and nitrogen) on the corrosion. High temperature here means in excess of 200 °C below which the corrosion rates are usually not appreciable.

2. High-temperature corrosion mechanism and kinetics

As discussed previously [14], if the diffusion process in the oxide is the rate-controlling step in high-temperature oxidation, then the oxidation rate obeys a parabolic rate law. In this case, the rate of change of the scale thickness is proportional to the scale thickness itself, i.e.

$$dx/dt = K_d/x \tag{1}$$

where x is the scale thickness, t the time, and K_d is constant controlled by the diffusion process. The parabolic rate law results from the parabola solution of Equation 1. On the other hand, if the metal surface or the phase boundary interface reaction is the rate-controlling step, then the oxidation rate does not change with time, i.e.

$$dx/dt = K_s' \tag{2}$$

where K_s' is a constant controlled by the metal surface or the phase interface reaction, and the oxidation obeys a linear rate law due to the linear line solution of Equation 2. If the diffusion of ions in the scale and the volatilization (and/or vaporization) of the scale occur simultaneously during oxidation, then oxidation is the superposition of Equations 1 and 2 except that the constant K_s' in Equation 2 is negative which means that volatilization results in the reduction of scale thickness, i.e. Equation 2 is modified as

$$dx/dt = -K_s \tag{3}$$

and the rate law equation is

$$dx/dt = K_d/x - K_s \tag{4}$$

This is the famous Tedmon equation [15].

However, this type of rate law plays an important role not in high-temperature oxidation, but in high-temperature chlorine corrosion (and even in halogen corrosion) due to the easier volatilization of most metal chlorides than their own oxides as described above. In this type of corrosion, the scale mentioned above is the chloride of the associated metal. The solution of Equation 4 is

$$t = -K_d/K_s^2\,[xK_s/K_d + \ln(1 - xK_s/K_d)] \tag{5}$$

provided the initial condition is that $x = 0$ at $t = 0$.

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TABLE I High-temperature chlorine environments summarized by Elliott *et al.* [11]

High temperature application	Temperature range (°C)	Type of corrosion
Mineral chlorination: precious metals, Ti and Zr production, chlorinators	300–900	Cl_2
High-temperature chlorination, reactors	<550	Cl_2
Vinyl chloride monomer production, ethylene dichloride cracker tubes	<650	Halide gas
Production of ethylene dichloride	280–480	HCl, air, ethylene
Titanium oxide production, heater tubes in $TiCl_4$ circuit	900	Cl_2 and oxidation
Aluminium melting, Mg removal by Cl_2 injection	< 850	Flue gases with Cl_2, HCl, sulphur, etc.
Fibreglass manufacturing, recuperators	< 900	Flue gases including halides and sulphides
Waste incineration,	< 850	Flue gases including Cl_2, and sulphur, etc.
Plant for H_2 from water	< 900	HCl
Power generation, boilers	< 950	Combustion gases including HCl, fuel ash, sulphate/chloride
Fluidized bed combustor, heat exchange tubes	850	HCl from coal with $CaSO_4$, CaO

In the initial period of attack or if the volatilization effect is not significant, the values of x and K_s are small compared with K_d, i.e. $xK_s/K_d \ll 1$, and $\ln(1 - xK_s/K_d)$ in Equation 5 can be expanded in power series. The result is

$$t \approx x^2/2K_d \qquad (6)$$

which approaches the general second-order parabolic rate law. In the growth period of metal chloride and if the volatilization effect is significant enough, obviously $xK_s/K_d \ll 1$ is no longer valid. Then the rate of change of the chloride thickness obeys Equation 5, i.e. the chloride produced from the ion diffusion volatilizes gradually during the corrosion. When the thickness approaches the value $x_f = K_d/K_s$, Equation 4 becomes $dx/dt = 0$ and the chloride does not grow further. Therefore, Equation 5 is available only at $x < x_f$. When x exceeds x_f, the volatilization at chloride/atmosphere interface will become the rate-controlling step and the linear rate law of corrosion, Equation 3, is satisfied. Thus, the total weight of the metal decreases gradually. From the discussion above, one can expect that the typical weight change of the metal with time is like curve A in Fig. 1, where x_f (or t_f), which was defined above the critical thickness (or time) when the scale no longer grows, depends on the temperature, atmosphere, and the chloride characteristics. The temperature always promotes the volatilization effect. If the growth of chloride is not fast enough to supply the amount required for volatilization, the corrosion rate law will obey Equation 3 (curve B, Fig. 1). For exmple, the corrosion of iron in 1.46 vol % HCl/N_2 (1 atm) at temperatures below 500 °C obeyed a parabolic rate law due to the formation of a protective $FeCl_2$ film on the metal surface [16]. As the temperature increased to 550 °C, the rate law was like curve A in Fig. 1. As it increased further to 800 °C, the rate law became like curve B. Similar kinetics also resulted for the corrosion of iron in 1 vol % Cl_2/N_2 (1 atm) except that the transition temperatures were different. Other investigations [5–9, 11, 17–28], using thermogravimetry techniques, also obtained corrosion kinetics typical of the curves of Fig. 1.

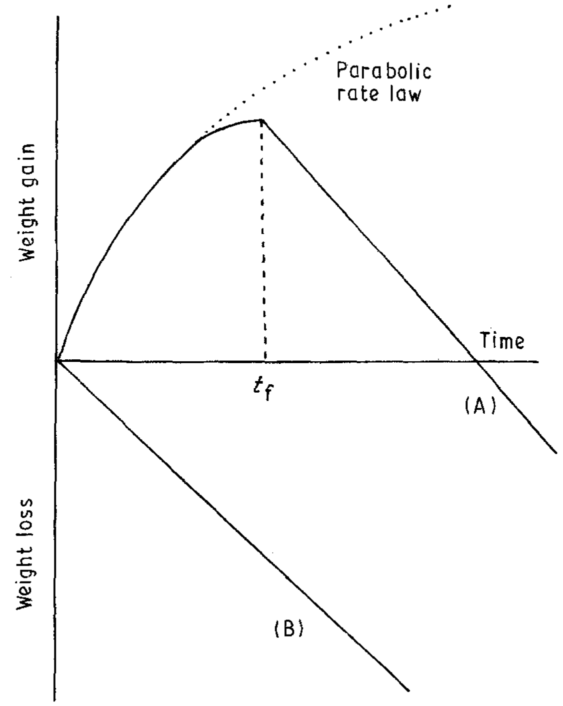

Figure 1 Typical curves of weight change of metal with time in high-temperature chlorine corrosion.

TABLE II Common binary metal chloride melting points (T_m) and temperatures (T_4) at which the chloride vapour pressure is 10^{-4} atm

Chloride	T_m (°C)	T_4 (°C)	Reference
$FeCl_3$	303	167	[12]
$FeCl_2$	676	536	[12]
$NiCl_2$	1030	607	[12]
$CoCl_2$	740	587	[12]
$CrCl_3$	1150	611	[12]
$CrCl_2$	820	741	[12]
$HfCl_4$	434	132	[12]
$PdCl_2$	678	474	[12]
$ThCl_4$	770	564	[29]
$CeCl_3$	800	911	[29]

Usually the diffusion of ions in chloride is fast enough only at temperatures above $0.5T_m$, where T_m is the melting point of the chloride. Furthermore, volatilization is significant only at vapour pressures above 10^{-4} atm. Table II lists the T_m and T_4 (the temperature at which the vapour pressure is 10^{-4} atm) values of some common metal chlorides summarized previously [12, 29]. However, we believe that T_4 plays a more important role than T_m in high-temperature chlorine corrosion.

3. Thermodynamic considerations

In high-temperature oxidation, the temperature dependence of the free energies of formation of oxides (Ellingham diagram) play an important role because one can predict the stable oxides at a particular temperature. Similarly, in high-temperature chlorine corrosion, stable chlorides can also be predicted from their free energies of formation as discussed earlier [12, 13]. However, in a mixture of more than one gas component, the situation is more complex. For example, considering pure iron in the mixture of hydrogen chloride and oxygen, the possible reactions are as follows.

$$n\mathrm{Fe} + m/2\ \mathrm{O_2} = \mathrm{Fe}_n\mathrm{O}_m \quad (7)$$

$$\mathrm{Fe} + 2\mathrm{HCl} = \mathrm{FeCl_2} + \mathrm{H_2} \quad (8)$$

$$\mathrm{FeCl_2} + \mathrm{HCl} = \mathrm{FeCl_3} + 1/2\ \mathrm{H_2} \quad (9)$$

$$\mathrm{Fe} + 2\mathrm{HCl} + 1/2\ \mathrm{O_2} = \mathrm{FeCl_2} + \mathrm{H_2O} \quad (10)$$

$$\mathrm{FeCl_2} + \mathrm{HCl} + 1/4\ \mathrm{O_2} = \mathrm{FeCl_3} + 1/2\ \mathrm{H_2O} \quad (11)$$

$$1/3\ \mathrm{Fe_2O_3} + 2\mathrm{HCl} = 2/3\ \mathrm{FeCl_3} + \mathrm{H_2O} \quad (12)$$

$$\mathrm{FeCl_2} + 3/4\ \mathrm{O_2} = 1/2\ \mathrm{Fe_2O_3} + \mathrm{Cl_2} \quad (13)$$

$$2/3\ \mathrm{FeCl_3} + 1/2\ \mathrm{O_2} = 1/3\ \mathrm{Fe_2O_3} + \mathrm{Cl_2} \quad (14)$$

Fig. 2 shows the temperature dependence of the standard free energies of Reactions 7–14 calculated from the thermodynamic data [29]. From the diagram one can expect that, in pure HCl, $FeCl_2$ is formed by Reaction 8, but further chlorination (Reaction 9) is thermodynamically impossible. In contrast, when the reaction gases contain both HCl and O_2, the oxy-chlorination leads typically to the formation of $FeCl_3$ by Reaction 11 as well as the formation of $FeCl_2$ by Reaction 10, as demonstrated by Ihara *et al.* [17].

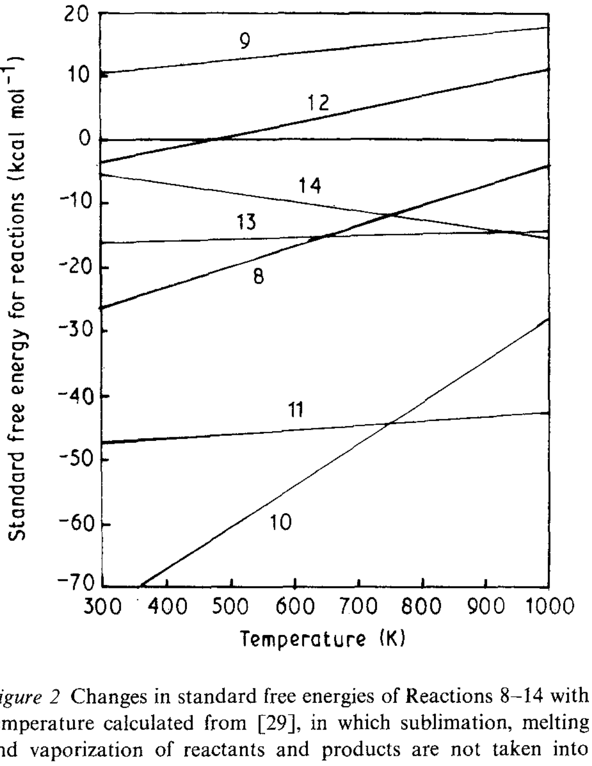

Figure 2 Changes in standard free energies of Reactions 8–14 with temperature calculated from [29], in which sublimation, melting and vaporization of reactants and products are not taken into account.

Similarly, the possible reactions of chromium in the mixture of HCl and O_2 are as follows.

$$2\mathrm{Cr} + 3/2\ \mathrm{O_2} = \mathrm{Cr_2O_3} \quad (15)$$

$$\mathrm{Cr} + 2\mathrm{HCl} = \mathrm{CrCl_2} + \mathrm{H_2} \quad (16)$$

$$\mathrm{CrCl_2} + \mathrm{HCl} = \mathrm{CrCl_3} + 1/2\ \mathrm{H_2} \quad (17)$$

$$\mathrm{Cr} + 2\mathrm{HCl} + 1/2\ \mathrm{O_2} = \mathrm{CrCl_2} + \mathrm{H_2O} \quad (18)$$

$$\mathrm{CrCl_2} + \mathrm{HCl} + 1/4\ \mathrm{O_2} = \mathrm{CrCl_3} + 1/2\ \mathrm{H_2O} \quad (19)$$

$$1/3\ \mathrm{Cr_2O_3} + 2\mathrm{HCl} = 2/3\ \mathrm{CrCl_3} + \mathrm{H_2O} \quad (20)$$

$$\mathrm{CrCl_2} + 3/4\ \mathrm{O_2} = 1/2\ \mathrm{Cr_2O_3} + \mathrm{Cl_2} \quad (21)$$

$$2/3\ \mathrm{CrCl_3} + 1/2\ \mathrm{O_2} = 1/3\ \mathrm{Cr_2O_3} + \mathrm{Cl_2} \quad (22)$$

Green sublimate corrosion product $CrCl_3 \cdot 6H_2O$ after the corrosion of chromium in HCl/20–75 vol % O_2 mixture at 550–800 °C observed [9] might come from the oxy-chlorination Reaction 19. Oxy-chlorination phenomena were also observed in other investigations [4, 5, 7, 8, 11, 18–23, 30–33].

4. Effects of gaseous components on the corrosion

Because many industrial atmospheres may also contain other flue gases in addition to Cl_2 and /or HCl, it is necessary to visualize the effects of these gaseous components on the chlorine corrosion. The role of chlorine itself in flue gas corrosion has been reviewed recently [13].

4.1. Oxygen and air

As described above, the reaction kinetics of iron in 1.46 vol % HCl/N_2 (1 atm) below 500 °C obeyed a parabolic rate law due to the protective $FeCl_2$ film. Ihara *et al.* [17] also found that in pure HCl gas at 300–800 °C, the corrosion behaviour was determined by the formation and sublimation of $FeCl_2$. Addition of 20–50 vol % O_2 to HCl greatly accelerated the corrosion because of the formation and sublimation of a low melting point volatile $FeCl_3$ via oxy-chlorination such as Reaction 11 described above. Similar results were also observed by the same investigators [7] on Fe–Ni alloys in the same gas mixture at temperatures greater than 500 °C and by Jacobson [18] on reaction of iron with 1 vol % HCl/0–50 vol % O_2/Ar mixture at 550 °C. Above 50 vol % O_2, the accelerating effect became less pronounced and it could even be reversed as shown in Fig. 3 [17] due to the formation of surface oxide films. In Cl_2, however, oxygen had little effect on the chlorination rate of iron below about 300 °C, although it prevented vaporization of $FeCl_3$ above this temperature due to the competitive formation of an iron oxide film too [34, 35].

In HCl gas the corrosion rate of chromium at 400–800 °C is determined by the formation and vaporization of $CrCl_2$ scale to some extent up to 600 °C.

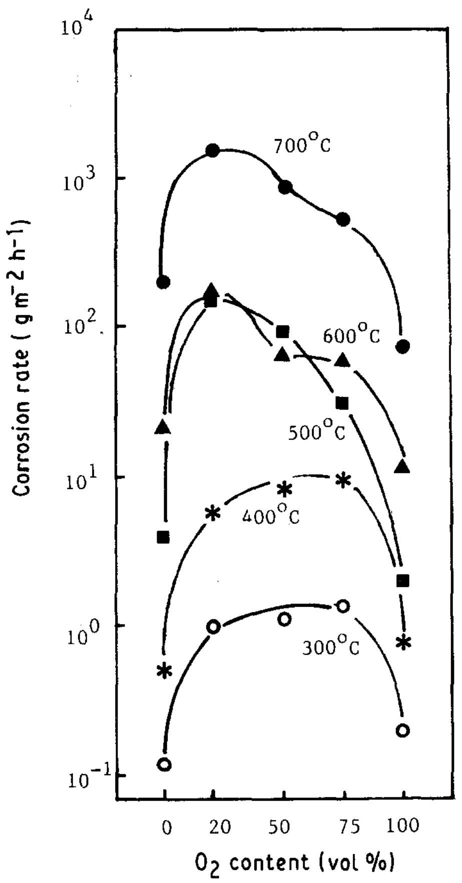

Figure 3 Change in average corrosion rates of iron in HCl, O_2 and their mixtures as a function of O_2 content, reproduced from [17]. The average corrosion rate was estimated from the weight loss after corrosion products were removed from specimens which were exposed to reaction gases for 5 h.

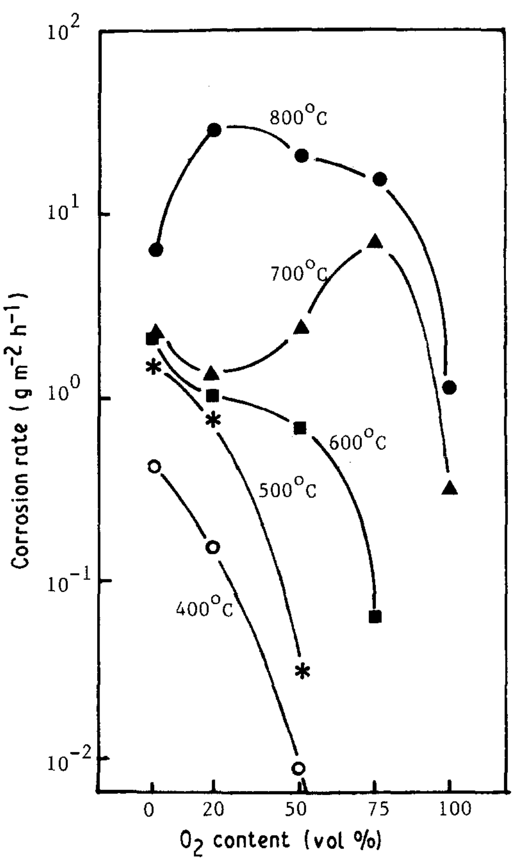

Figure 4 Changes in average corrosion rates of chromium in flowing HCl, O_2 and their mixtures as a function of O_2 content, reproduced from [9]. The average corrosion rate was estimated from specimens which were exposed to reaction gases for 5 h.

Addition of 20–75 vol % O_2 led to suppression of corrosion up to about 600 °C due to the formation of Cr_2O_3, but to catastrophic corrosion at higher temperatures as shown in Fig. 4 [9] due to the vaporization of $CrCl_3$ and water vapor which might also come from oxy-chlorination. In mixtures of Cl_2 and O_2, the corrosion of chromium was inhibited even at temperatures as high as 700 °C through the formation of an outer Cr_2O_3 layer and of CrO_2Cl_2 as the only volatile product [19].

The corrosion rates of Fe–Cr alloys in HCl at 500–650 °C are determined by the formation and sublimation of both $FeCl_2$ and $CrCl_2$. Because of the formation of a protective corundum-type oxide scale ($\alpha - [Fe(Cr)]_2O_3$) on alloys with chromium content $\geqslant 13$ wt %, addition of 20–50 vol % O_2 effectively suppressed the corrosion at relatively low temperatures [8]. This type of corundum-type oxide scale was also observed on austenitic stainless steels at 450–500 °C in the same range of gas mixtures [5]. The temperature range for the protective scale formation is raised with increasing chromium content in the alloy and oxygen content in the gas mixture. Further rise in temperature accelerates corrosion due to sublimation of $FeCl_3$ and $CrCl_3$ as a result of oxy-chlorination. For example, the oxide scale $[Fe(Cr)]_2O_3$ formed on Fe–13 wt % Cr alloy above 500 °C in 80 vol % HCl + 20 vol % O_2 was depleted of chromium due to the sublimation of $CrCl_3$, and became less protective [8]. No data on corrosion of Fe–Cr alloys in gas mixture of Cl_2 and O_2 have been published.

The oxy-chlorination products of molybdenum are very volatile. Therefore, the corrosion rate of SUS 316 steel in gas mixtures of HCl and 20–50 vol % O_2 at temperatures lower than 420 °C was reported to be significantly high [5] because the protective scale became defective by sublimation of the oxy-chlorides of molybdenum. At still higher temperatures the detrimental effect of molybdenum in the steel was not significant because all the alloy constituents also suffered oxy-chlorination in the high-temperature range.

Because of exclusive formation of $NiCl_2$ scale at 400–700 °C, the presence of oxygen in HCl-containing atmospheres, regardless of the gas compositions, appears to have a negligible effect on corrosion of nickel as demonstrated by Ihara *et al.* [6]. But its attack at 927 °C was predicted by McNallan and Liang [36] to decrease with increasing oxygen partial pressure in chlorine environments. Corrosion in gas mixture of Cl_2 and O_2 at lower temperature, as in the case of pure HCl, proceeds mainly via formation and volatilization of $NiCl_2$. However, at much higher temperatures the rate of corrosion of nickel in Cl_2 is considerably accelerated by the presence of oxygen probably due to the following two reactions

$$2\,Ni_{(s)} + Cl_{2(g)} = NiCl_{ads} \qquad (23)$$

$$2\,NiCl_{ads} + 1/2\,O_{2(g)} = 2\,NiO_{(s)} + NiCl_{2(g)} \qquad (24)$$

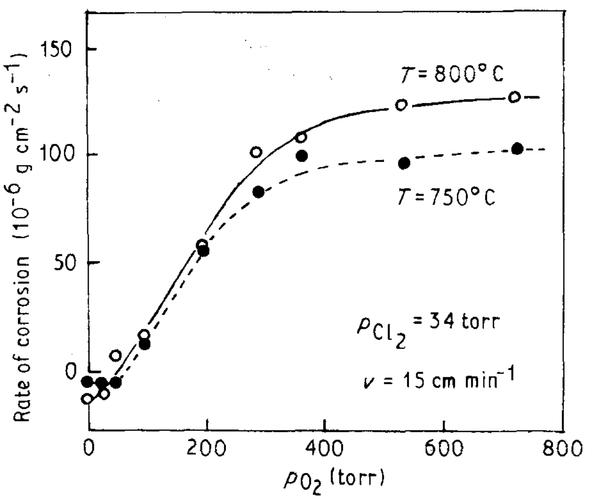

Figure 5 Effect of O_2 pressure on corrosion of Ni in Cl_2 at 750 and 800 °C [37]. 1 torr = 1.333×10^2 Pa.

The mechanism described by these reactions involves formation and oxidation of NiCl which was detected spectroscopically to be formed as an intermediate at high temperatures [37]. The accelerating effect of oxygen on chlorination of nickel at higher temperatures is illustrated by Fig. 5 reproduced from [37].

In summary, the effect of oxygen is to produce an oxide scale or oxy-chloride scale. Oxides are beneficial to the corrosion resistance. However, the effect of oxy-chloride is detrimental if it is more volatile than the scale produced from the atmosphere without oxygen, while it is beneficial if it is less volatile.

The effect of air on corrosion seems similar to that of oxygen. An additional observation is that found by Elliott *et al.* [21, 23] on aluminium-containing alloy in air/2 vol % Cl_2 mixture at 900 and 1000 °C. Alumina (Al_2O_3) is preferentially formed by air and the formation of volatile $AlCl_3$ is inhibited. The corrosion rate of the alloy is thus reduced. However, we expect that this phenomenon would also occur in mixtures of oxygen and chlorine.

4.2. Water vapour

The effect of water vapour on the chlorine corrosion was examined early in 1956 [34, 38], and was found that the corrosion rates of most tested metals, such as iron and its alloys, stainless steels, aluminium, and tantalum, were greatly diminished in the presence of water vapour because of the protective oxide film up to a certain limiting temperature. Recently, Gesmundo *et al.* [39] also reported that, during the corrosion of ternary Ni–29Mo–4Fe alloy, water vapour in an HCl-containing atmosphere promoted the formation of NiO and inhibited the formation of $NiCl_2$. A similar phenomenon was also expected during the corrosion of Ni-containing alloy Hastelloy B [40]. All these phenomena might be attributed to the fact that oxides of most metals are more stable than their own chlorides [12, 41]. However, during the corrosion of Ni–Cr–Al alloy in HCl-containing moist air [42, 43], NiO was permeable to water vapour and impermeable to hydrogen. Therefore, H_2O penetrated from the atmosphere through the outer NiO layer to react with inner Al and Cr. The reaction product H_2 resided at the alloy/oxide (Al_2O_3, Cr_2O_3) interface and induced oxide cracking when it attained a certain partial pressure. Spalling of the oxide corrosion products was also observed during the corrosion of Incoloy 800 (32Ni–21Cr–46Fe) in moist air containing HCl at 800 °C [31]. But no direct evidence can demonstrate that it came from H_2O or from HCl.

4.3. Sulphur dioxide and nitrogen

Woodford and Bricknell [44] found that penetration and embrittlement of grain boundaries by sulphur occurred in nickel and nickel-base superalloy. It affected not only the corrosion of flue gas at 900 °C but also the mechanical properties of the materials. It was also observed [1] that 0.18 vol % SO_2 in HCl-containing flue gas promoted susceptibility to cracking at 540 °C of ferritic steels by formation of FeS at the metal/scale interface and of austenitic steels by sulphur segregation at grain boundaries. However, Prescott and co-workers [33, 45] reported that 0.86 vol % SO_2 in HCl-containing flue gas did not affect the corrosion of metals and alloys at 900 °C, because the partial pressure of sulphur in that environment was too low to form sulphide at that temperature. In addition, 0.5 vol % SO_2 in a combustion HCl-containing flue gas probably did not affect the corrosion of mild and low alloy steels at 400–500 °C although the metallographic examination revealed FeS in the outer parts of the scale [46].

The effect of other flue gas such as nitrogen is dilution of chlorine only and the corrosion is thus reduced as reported much earlier [35].

5. Conclusions

1. High-temperature corrosion consists mainly of the diffusion of ions in the scale and the volatilization of the scale. The rate-controlling step from the corrosion kinetics which results from the Tedmon equation can be determined.
2. In a mixture of more than one gas component, free energies of formation of all possible reactions should be considered for prediction of reaction products from the thermodynamic viewpoint. Oxy-chlorination often occurs in those chlorine atmospheres containing oxygen.
3. Effect of oxygen and/or air is to produce an oxide scale or oxy-chloride scale. Oxides are beneficial to the corrosion resistance. However, the effect of oxy-chloride is detrimental if it is more volatile than the scale produced from the atmosphere without oxygen, while it is beneficial if it is less volatile. In some cases alumina is preferentially formed by oxygen and the formation of volatile $AlCl_3$ is inhibited.
4. Effect of water vapour on the corrosion resistance of most metals is beneficial due to the formation of a protective oxide. However, in some cases such as Ni–Cr–Al alloy in HCl-containing moist air [42, 43], oxide cracking can occur due to the hydrogen produced from the reaction of H_2O with Al and Cr at the alloy/oxide interface.

5. In some cases, sulphur dioxide is detrimental to the chlorine corrosion resistance because of the susceptibility to embrittlement or cracking, while in other cases it does not affect the corrosion. Effect of nitrogen is dilution of chlorine only and the corrosion rate is thus reduced.

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