CHAPTER 1

Thermodynamics and Kinetics of the High Temperature Oxidation of Stainless Steels

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Abstract. This chapter introduces stainless steels and their classification for the high temperature applications. The enabling theories for the high temperature corrosion i.e. thermodynamics and kinetics are further addressed. The basic concept of thermodynamics is given and the stability of the formation of thermal oxide on stainless steel is exemplified. Types of defect in the oxide and Fick's first law for the diffusion of defect through the oxide are introduced. Oxidation kinetics is explained with the emphasis on the derivation of the parabolic rate law.

1.1 Introduction to Stainless Steels

As noted by A. Galerie [1], the first idea of producing stainless steel might trace back to the year 1882 when the French metallurgist P. Berthier recorded that the sufficient addition of chromium to iron could make the steel better resistant to the corrosion in water and acid. However, such steel with good enough mechanical stability had not been realised until H. Brearley from Sheffield produced the first stainless steel containing 13 wt.% of chromium and 0.24 wt.% of carbon in 1913 [1]. The commonly used AISI 304 stainless steel was produced by W.H. Hatfield in 1924 [1].

Nowadays stainless steel is defined as a ferrous alloy containing chromium with a minimum content of about 10.5–12 wt.% [2, 3], while it is suggested that the chromium content to combat the high temperature corrosion should be at least 18 wt.% [4, 5] if other elements beneficial to the use in this condition are not additionally alloyed. The classification of stainless steels is normally based on its structure which closely relates to the steel mechanical properties e.g. ferritic, austenitic, martensitic, austeno-ferritic (duplex) or precipitation-hardened stainless steels. Some elements are added to the steel and have the effect on stabilising the ferrite matrix e.g. chromium, molybdenum, silicon and niobium [4], while some elements stabilise the austenite matrix e.g. nickel, manganese, nitrogen and carbon [4, 6]. For example, the AISI 304 grade which has the austenite structure at room temperature is obtained by the addition of 9.5 wt.% of nickel to the ferritic Fe–19Cr (unless mentioned otherwise, the chemical composition is in wt.%) [1, 7].

However, in the high temperature corrosion aspect, stainless steels are typically classified by the type of the thermal oxide scale formed at high temperatures i.e. chromia- or alumina-forming ones. Table 1.1 lists chemical compositions of some important chromia- and alumina-forming stainless steels. It is noted that, for titanium and niobium contents which are reported as a range, the lower limit is in fact a function of carbon and nitrogen contents in the steel [7], but in this table it is calculated by using the maximum content of carbon and neglecting the nitrogen content.

Table 1.1 Chemical compositions (wt.%) of stainless steels.

Stainless steel	The first group			The second group		The third group (reactive element)					Ni	Mn	Mo	C	Refs.	
	Cr	Al	Si	Ti	Nb	Y	Zr	Hf	Ce							
Chromia-forming stainless steel																
409	10.5–12.5		<1	0.18–0.65							1			<0.03	[3, 7, 8]	
430	16–18		<1								1			<0.08	[7, 8]	
430Ti	16–18		0.62	0.45							0.42			0.04	[7, 9]	
441	17.5–18.5		<1	0.1–0.6	0.39–1						1			<0.03	[3, 7]	
444	17–20		<1	0.25–0.8							1	1.8–2.5		<0.025	[3, 7]	
446	23–26		<1								1.5			<0.1	[7, 8]	
304	18–20		0.75								2			0.08	[1, 3]	
316	16–18		0.75								2	2–3		<0.08	[1, 3]	
309	22–24		1								2			0.2	[8]	
310	24–26		1.5								2			0.25	[8]	
321	17–19		<1	0.05–0.8							2			<0.1	[7, 8]	
12SR	12	1.2	0.6	0.3	0.6									<0.04	[7]	
18SR	17–18	1.7–2.1	<1	0.36–0.8										<0.04	[7]	
Alumina-forming stainless steel																
Ohmalloy 30	12.6	2.6	0.3	0.3							0.6	0.4		0.02	[10]	
Ohmalloy 40	12.7	3.6	0.2	0.3							0.5	0.4		0.02	[10]	
ODM751	16.1	5	0.04	0.56		0.4					0.02		1.5	0.01	[10]	
SUH21	17.7	3	0.3	0.1					0.01		0.1	0.1		0.01	[10]	
MA956	19.2	4.3		0.36		0.63 Y ₂ O ₃								0.01	[11]	
PM2000	18.9	5.1	0.04	0.45		0.37 Y ₂ O ₃					0.01	0.11		0.01	[11]	
APM	20.4	5.5	0.2	0.03			0.1				-	0.08		0.03	[11]	
APMT	22	5	≤0.7	0.02		0.1	0.05	0.1				≤0.4	3	<0.05	[12]	
MA956HT	21.7	5.8	0.05	0.4		0.38 Y ₂ O ₃					0.11	0.06		0.03	[11]	
Aluchrom YHf	20.3	6.1	0.2			0.06	0.05	0.03			0.1	0.2		0.02	[10]	

The maximum service temperature of the steel depends on many factors especially the composition of the hot gas and the loading condition at high temperatures. However, a primary guidance for the maximum use temperature of some stainless steels for isothermal oxidation is shown in Table 1.2. For each steel grade in this table, only important elements especially the ones that help increase the high temperature corrosion resistance are listed with the contents averaged from the values reported in Table 1.1.

Table 1.2 Maximum isothermal service temperatures ($T_{\max}$) of stainless steels [1, 7, 13].

$T_{\max}$ (°C)	Stainless steel grade		
	Chromia former		Alumina former
	Ferritic grade	Austenitic grade	
750	430 (Fe–17Cr)		
800	409 (Fe–11Cr–0.42Ti)		
815	430Ti (Fe–17Cr–0.45Ti)		
850		304 (Fe–19Cr–9.5Ni) 316 (Fe–17Cr–12Ni–2.5Mo)	
950	441 (Fe–18Cr–0.35Ti–0.7Nb) 444 (Fe–18.5Cr–0.53Ti–2.15Mo)		
1000		309 (Fe–23Cr–13.5Ni–1Si)	
1150	446 (Fe–24.5Cr)	310 (Fe–25Cr–20.5Ni–1.5Si)	
1200			Aluchrom YHf (Fe–20.3Cr–6.1Al– 0.06Y–0.05Zr– 0.03Hf)
1300			MA956 (Fe–19.2Cr–4.3Al– 0.36Ti–0.63 Y ₂ O ₃)

For the chromia-forming stainless steels, we might consider that the basic grade for the high temperature application is an AISI 430 ferritic stainless steel which consists of about 16–18 wt.% of chromium and has the maximum isothermal use temperature of 750 °C. The addition of some alloying elements could increase the high temperature corrosion resistance and therefore the maximum use temperature. Mechanisms of the alloying elements to help reduce the stainless steel oxidation rate are explained in Chapter 4. However, the empirical observation of this effect especially from Tables 1.1 and 1.2 may be noted here as follows.

The first group of the elements that can help increase the high temperature corrosion resistance consists of chromium, aluminium and silicon. These elements could react with oxygen and form the protective oxide layer [1, 4, 5] or internal precipitates [14] that make the steel resistant to the high temperature oxidation. For example, when comparing with AISI 430 (Fe–17Cr), the addition of chromium up to 23–26 wt.% in the steel gives AISI 446 which has the maximum isothermal use temperature up to 1150 °C. The increase in chromium content from 18–20 wt.% in AISI 304 to 22–24 wt.% in AISI 309 and the increase in silicon content from 0.75 wt.% in AISI 304 to 1 wt.% in AISI 309 significantly increases in the maximum isothermal use temperature from 850 °C for AISI 304 to 1000 °C for AISI 309. The addition of aluminium by 1.2 wt.% to Fe–12Cr, giving 12SR stainless steel, could form the internal alumina precipitate at the interface between the chromia scale and steel substrate and therefore allows the maximum isothermal use temperature up to 900 °C [1, 7]. It is noted that 12SR and 18SR are chromia-forming stainless steels when they are oxidised

in air [1]. However, in a more reducing atmosphere chromia may become unstable and in this situation these alloys could turn to be the alumina-formers [1].

The second group of the elements beneficial to the high temperature corrosion is titanium and niobium. These elements are primarily added to the steel to avoid chromium carbide formation thus mitigating the sensitisation problem of the steel [4, 8]. However, as will be explained in Chapter 4, the addition of these elements could also promote the high temperature corrosion resistance. For example, the addition of 0.18–0.65 wt.% of titanium to Fe–11.5Cr makes AISI 409 which has the maximum isothermal use temperature of 800 °C. This temperature is higher than the one of AISI 430 which contains higher chromium content (16–18 wt.%) but is not stabilised by titanium. The addition of 0.45 wt.% of titanium to AISI 430 gives the 430Ti grade which has the higher maximum isothermal use temperature up to 815 °C [1, 13]. The slight increase in chromium from 16–18 wt.% in AISI 430 to 17.5–18.5 wt.% in the 441 grade with the stabilisation by titanium and niobium increases the maximum isothermal use temperature of the steel up to 950 °C.

For the alumina-forming stainless steel, aluminium must be sufficiently added to the Fe–Cr so that the stable continuous alumina layer can be formed. Once the alumina forms the oxidation rates of the steels tend to be improved compared to those of the chromia-forming stainless steels. This is because alumina has very low deviation from stoichiometry, i.e. this deviation is about 10^{-3} for chromia at 600 °C while it is about 10^{-4} for alumina even at 1000 °C [13]. Furthermore, the cation self-diffusion coefficient at 1000 °C in alumina is about $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ while that of the chromia is higher i.e. $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at the same temperature [13]. From Tables 1.1 and 1.2 it can be seen that by adding aluminium to form the alumina protective layer together with the addition of titanium and/or reactive elements e.g. yttrium, zirconium, hafnium and cerium, the alumina-forming stainless steels can be used at temperatures higher than 1000 °C. For example, the addition of 6.1 wt.% aluminium with small amounts of yttrium, zirconium and hafnium to Fe–20.3Cr gives Aluchrome YHf which has the maximum isothermal use temperature of 1200 °C. The addition of 4.3 wt.% of aluminium, 0.36 wt.% of titanium and 0.63 wt.% of Y_2O_3 to the Fe–19.2Al gives the oxide-dispersion strengthened (ODS) MA956 stainless steel which can be used isothermally at temperatures up to 1300 °C.

From this introduction, it can be seen that we need to know that when stainless steels with different chemical compositions are used at high temperatures under atmospheres with different gas compositions, which oxide phases are stable and could be formed. Furthermore, with these oxides, what the reaction rate and mechanism are. To answer these questions, we need thermodynamics to understand stability of the phases formed and we need kinetics to identify the rate and the oxidation mechanisms. The basics of these subjects will be given in the following sections.

1.2 Thermodynamics of the High Temperature Corrosion

1.2.1 Basic Concepts

The prediction of oxide formation requires to determine the most stable states of the reacting system. At constant temperature and pressure, the stability of a system is measured by its Gibbs free energy. The total Gibbs free energy, G , of a system is defined as

$$G = H - TS = U + PV - TS \quad (1.1)$$

where H is the enthalpy, S the entropy, U the internal energy, V the volume of the system, P the pressure and T the temperature.

The Gibbs free energy change, dG , for a system in which change of composition takes place through chemical reaction, is given by

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} dn_i = VdP - SdT + \sum_i \mu_i dn_i \quad (1.2)$$

where n_i is the mole number of component i and $\mu_i = (\partial G / \partial n_i)_{P, T, n_{j \neq i}}$ the chemical potential.

The general expression of chemical potential of the component i is given by

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (1.3)$$

where μ_i° is the standard chemical potential and a_i the activity of compound i .

Change in mole number of component i can be expressed from the extent of reaction (ξ) and the stoichiometric coefficient (ν_i), which are negative for reactants and positive for products of the reaction, i.e.

$$dn_i = \nu_i \cdot d\xi \quad (1.4)$$

The combination of Eqs. 1.2 and 1.4 yields

$$dG = VdP - SdT + \sum_i \mu_i \nu_i d\xi = \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP + \left(\frac{\partial G}{\partial \xi} \right)_{P, T} d\xi \quad (1.5)$$

and hence

$$\left(\frac{\partial G}{\partial \xi} \right)_{P, T} = \sum_i \nu_i \mu_i = \Delta_r G \quad (1.6)$$

$\Delta_r G$ is the change in the Gibbs free energy of a system that occurs during a reaction. Equilibrium and spontaneity criteria are defined from the second law of thermodynamics as follows.

For the case I, equilibrium is achieved at constant pressure and temperature when G is minimised, i.e. $(dG)_{P, T} = 0$ or $\Delta_r G = 0$ from Eqs. 1.5 and 1.6.

For the case II, a system proceeds spontaneously during a reaction at constant pressure and temperature when $(dG)_{P, T} < 0$ or $\Delta_r G < 0$.

We consider an oxidation reaction of a metal M such as

From Eqs. 1.3 and 1.6, the expression of Gibbs free energy of reaction is written as follows:

$$\Delta_r G = \sum_i \mu_i \nu_i = \frac{2}{b} \mu_{M_a O_b} - \frac{2a}{b} \mu_M - \mu_{O_2} = \frac{2}{b} \mu_{M_a O_b}^\circ - \frac{2a}{b} \mu_M^\circ - \mu_{O_2}^\circ + RT \ln \frac{a_{M_a O_b}^{2/b}}{a_M^{2a/b} \cdot a_{O_2}} \quad (1.8)$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{a_{M_a O_b}^{2/b}}{a_M^{2a/b} \cdot a_{O_2}} \quad (1.9)$$

According to the second law, when equilibrium is achieved, Eq. 1.9 becomes

$$\Delta_r G^\circ = -RT \ln \frac{(a_{M_a O_b}^{2/b})_{eq}}{(a_M^{2a/b})_{eq} \cdot (a_{O_2})_{eq}} = -RT \ln K \quad (1.10)$$

where $\Delta_r G^\circ$ is the standard Gibbs free energy of reaction and K the equilibrium constant used to describe the equilibrium state of the reaction system.

1.2.2 Construction and Use of Thermodynamic Diagrams

Diagrams allow determination of the oxide likely to form during selective oxidation of alloys for given operating conditions. The Ellingham diagram, i.e. the plot of the standard Gibbs free energy of reaction ($\Delta_r G^\circ$) *versus* temperature, is useful to compare the relative stabilities of each oxide.

From Eq. 1.1, the standard Gibbs free energy of reaction $\Delta_r G^\circ$ is written as follows:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \quad (1.11)$$

$\Delta_r H^\circ$ and $\Delta_r S^\circ$ are calculated in temperature range without change of state from standard molar heat of formation and molar entropies assuming that the heat capacity contribution is negligible. From Eq. 1.11, $\Delta_r G^\circ$ can be plotted as a linear function of T , giving the Ellingham diagram as shown in Fig. 1.1. The $M/M_a O_b$ line in the diagram indicates the oxidation reaction in the form of Reaction 1.7 which is normalised to consume one mole of O_2 . Because the values of $\Delta_r G^\circ$ are expressed in kJ per one mole of the oxygen gas so the stabilities of various oxides can be compared directly, i.e. the lower the position of the line on the diagram, the more stable is the oxide. If the activities of M and $M_a O_b$ are taken as unity (i.e. pure condensed phases), Eq. 1.10 can be used to express the activity or the partial pressure of oxygen at which the metal and the oxide coexist. Then the dissociation pressure of the oxide $(p_{O_2})_{eq}$ can be calculated as follows:

$$(a_{O_2})_{eq} = \frac{(p_{O_2})_{eq}}{p^\circ} = \exp\left(\frac{\Delta_r G^\circ}{RT}\right) \quad (1.12)$$

where p° is the standard pressure equalling to 1 bar.

From Eqs. 1.9 and 1.12, expression of Gibbs free energy of reaction is established as follows:

$$\Delta_r G = \Delta_r G^\circ - RT \ln \frac{p_{O_2}}{p^\circ} = RT \ln \frac{(p_{O_2})_{eq}}{p_{O_2}} \quad (1.13)$$

Equilibrium and spontaneity criteria relying on the second law are deduced from Eq. 1.13. If the oxygen partial pressure p_{O_2} is higher than the equilibrium value $(p_{O_2})_{eq}$, the metal will be oxidised ($\Delta_r G < 0$), and if it is lower than the equilibrium value then the oxide will be reduced ($\Delta_r G > 0$). For a given temperature T , the value of $(p_{O_2})_{eq}$ can be determined directly from the Ellingham diagram by drawing a straight line from the origin marked Ω ($T = 0$ K and $\Delta_r G^\circ = 0$) through the point of the $M/M_a O_b$ line at the temperature of interest T and reading the oxygen partial pressure from its intersection with the logarithmic scale at the right side labelled $\log(p_{O_2})_{eq}$ (Fig. 1.1). This

$\log(p_{\text{O}_2})_{\text{eq}}$ scale is built from a network of straight lines radiating from the origin Ω and corresponding to $RT \ln((p_{\text{O}_2})_{\text{eq}} / p^\circ)$.

Fig. 1.1. Ellingham diagram for selected oxides constructed using thermodynamic data from Kubaschewski et al. [15].

The second type of diagram is the stability diagram of condensed phases. It relies on Eq. 1.14 and consists to plot $\log(p_{\text{O}_2})_{\text{eq}}$ with $(p_{\text{O}_2})_{\text{eq}}$ in bar *versus* the reciprocal temperature, as presented in Fig. 1.2 plotted using data from Ref. [16].

$$\log(p_{\text{O}_2})_{\text{eq}} = \frac{\Delta_r G^\circ}{(\ln 10)RT} = \left(\frac{\Delta_r H^\circ}{10^4 (\ln 10)R} \right) \cdot \frac{10^4}{T} - \frac{\Delta_r S^\circ}{(\ln 10)R} \quad (1.14)$$

Fig. 1.2. Stability diagram of oxides calculated using FactSage and FactPS database (FactSage 7.0) [16].

For instance, for a usual stainless steel, AISI 304L (Fe–17.5Cr–8Ni–1.72Mn–0.32Si–0.02C) [17], diagram in Fig. 1.2 indicates that MnO and SiO₂ can be formed selectively under Cr₂O₃ as shown in the upper figure of Fig. 1.3. Depending on the activity and diffusion coefficient of these elements in the metal, but also depending on the solubility and diffusivity of oxygen, these oxides can precipitate internally or form a continuous layer.

According to the diagram in Fig. 1.2, the oxide MnO is more stable than Cr₂O₃ and might be expected to form a sublayer beneath a Cr₂O₃ scale. This does not occur for several reasons. Firstly, MnCr₂O₄ spinel-type oxide is stable with respect to the binary oxides (MnO and Cr₂O₃) at high temperature. Secondly, manganese is soluble and diffuses rapidly in Cr₂O₃ but relatively slowly in the alloy [18]. Then, the duplex oxide scale MnCr₂O₄/Cr₂O₃ is commonly observed on manganese-containing stainless steels as shown in the lower figure of Fig. 1.3. The cross-section micrograph of AISI 304L oxidised at 850 °C in O₂ in Fig. 1.4 reveals this typical duplex microstructure. When duration or temperature increases, fast growing iron-rich nodules appear and the oxide scale is no longer protective [17].

Even if the diagrams in Figs. 1.1 and 1.2 allow to explain the successive oxide formed from the oxide/gas interface to the metal/oxide interface, a more realistic approach is required because activity of elements is not equal to unity in the alloy, and mixed oxide (e.g. MnCr₂O₄) and solid solution oxide (e.g. Cr_{2–x}Fe_xO₃) must be taken into account. Thermo-Calc software package [19] in combination with the suitable database can be used for thermodynamic calculations, based on the CALculation of PHase Diagram (CALPHAD) method. The calculation of phase equilibria in a multicomponent system requires the total Gibbs free energy minimisation of the system. The CALPHAD method employs various phenomenological models (e.g., substitutional solution model for most of the disordered solution phases, sub-lattice model for phases composed of several sub-lattices on which the various components can mix as for carbides...) to describe the temperature,

pressure, and concentration dependencies of the Gibbs free energy functions of each phase that takes part in the equilibrium and to assign them an analytic expression. The assessed parameters for thermodynamic models for the individual phases, evaluated that the model fits the available experimental data for a given phase, are stored in thermodynamic databases linked to software for minimisation process and the calculation of phase equilibria. In fact, accuracy of calculations is dependent on the databases behind the package. A complete description of the CALPHAD technique can be found in literature [20, 21].

Fig. 1.3. Schematic sketch of the oxide scale grown on the AISI 304L stainless steel.

Fig. 1.4. SEM-BSE cross-section micrograph (upper picture) and EDX element mapping after oxidation (lower picture) of the AISI 304L stainless steel oxidised at 850 °C in oxygen. Reproduced and adapted from A. Col et al., Corros. Sci. 114 (2017) 17–27 [17].

For instance, for the AISI 304L stainless steel oxidised at 850 °C in oxygen, the TCFE database devoted to steels and Fe-base alloys is used [17]. Useful diagrams consist to plot the fractions of phase and the composition of each phase *versus* O_2 activity as shown in Fig. 1.5. According to Fig. 1.5(a), once the corundum-type oxide M_2O_3 is formed, the oxygen partial pressure at the metal/oxide interface decreases to 10^{-26} bar. Oxygen partial pressure is then controlled by the decomposition pressure of the corundum oxide, which is Cr_2O_3 according to Fig. 1.5(b). Figs. 1.5(b) and (c) show the evolution of spinel and corundum oxide composition depending on oxygen activity. The iron enrichment of both oxides corresponds to an increase of oxygen activity and then to a less protective oxide scale.

Fig. 1.5. (a) Volume fraction of phases, (b) atomic fraction of elements in corundum, and (c) atomic fraction of elements in spinel at different oxygen activities for AISI 304L oxidised at 850 °C in oxygen. Redrawn and adapted from A. Col et. al., Corros. Sci. 114 (2017) 17–27 [17].

1.3 Point Defects in Metal Oxide

The former section assumes that the interested material is a kind of bulk without defects. However, the oxide always contains defects, and importantly the growth of thermal oxide on metal consists of elementary steps including the diffusion process relevant to these defects. This section introduces the formation of point defects in the oxide by the interaction with oxygen gas in the atmosphere which could lead to the scenarios of the possible mechanisms of the oxide growth.

At high temperatures, metal is oxidised by the hot gas giving thermal oxide scale on its surface. The global reaction for the oxidation of metal (M) with oxygen gas (O₂) resulting in the metal oxide (M_aO_b) is as follows:

The oxidation mechanism may start from the adsorption of the gas molecule from the atmosphere on the surface. An example of the surface reaction is Reaction 1.16 which is the dissociative adsorption of oxygen on the oxide/gas interface [13]. The s notation denotes an unoccupied site on the oxide/gas interface and O-s represents the adsorbed oxygen at that interface.

For the inward growth of a compact oxide, after the adsorption process the adsorbed oxygen is incorporated into the oxide possibly by jumping into the oxide lattice or the oxide grain boundary. It therefore diffuses via these paths from the external oxide/gas to the internal metal/oxide interface. For the transport through the oxide lattice, the diffusion may occur by the jumping of oxygen vacancy or oxygen interstitial.

The vacancy at the oxygen site is simply called an *oxygen vacancy* and denoted as V_O. If two electrons are still localised at the oxygen vacancy site, the effective charge which is the charge of the present defect (-2) relative to the charge of oxygen in a perfect crystal (-2) will be zero. If the oxygen vacancy is formed with a loss of one electron, the actual charge of the defect will be -1, giving the effective charge of +1. In such case we may describe the defect as V_O[•] where one dot superscript denotes the effective charge of +1. This defect may also be described in general as V_O^{z•} where z is a degree of ionisation (0 ≤ z ≤ 2 for oxygen). As for the oxidation mechanism, this defect is formed at the internal interface by the following reaction:

where <M> is the metal in the substrate, M_M is the metal on the normal metal lattice site in the oxide, and e' is the electron. After the formation of the oxygen vacancy at the internal interface, oxygen on the oxygen site of the oxide jumps into this oxygen vacancy inwardly, resulting in the outward diffusion of the oxygen vacancy to the external interface. At the external interface, the adsorbed oxygen according to Reaction 1.16 jumps into the oxygen vacancy according to Reaction 1.18:

If it is assumed that the rate constants of the interfacial forward Reactions 1.16, 1.17 and 1.18 are very rapid compared with the diffusion rate through the oxide, these reactions thus attain equilibrium [13]. As a result, Reactions 1.16 and 1.18 which take place at the external interface can lead to Reaction 1.19. Fig. 1.16 (case I) schematises the possible oxidation mechanism by the oxygen vacancy for the growth of the metal oxide MO. The mentioned assumption will also be applied to the other three following cases where the oxygen interstitial, metal vacancy or metal interstitial are dominant.

As for the oxygen interstitial, the oxygen that occupies an interstitial site is called an *oxygen interstitial* and denoted as $O_i^{z'}$ where one prime notation represents one negative effective charge. At the external interface, oxygen gas jumps into the oxide and forms the oxygen interstitial with electron hole ($h^\bullet$) according to Reaction 1.20:

Then it diffuses inwards to form the oxide at the internal interface by the following reaction:

Fig. 1.6 (case II) schematises the oxidation mechanism by this defect for the growth of MO.

For the outward growth of the compact scale, the metal from the substrate diffuses from the internal to the external interface in order to react with oxygen in the atmosphere giving the new construction unit of metal oxide at the external interface. For the diffusion through the oxide lattice, firstly through the metal vacancy $V_M^{z'}$ where $0 \leq z \leq$ higher oxidation state of M, this defect is formed at the external interface by the following reaction:

Thermal oxide is grown by the outward jumping of metal on the metal site of oxide to the metal vacancy, resulting in the inward diffusion of metal vacancy through the oxide to the internal interface. At the internal interface, the defect is annihilated by the following reaction:

The oxidation mechanism by this defect for the growth of MO is sketched in Fig. 1.6 (case III).

For the last case, the metal may jump into the interstitial site giving *metal interstitial* $M_i^{z\bullet}$, this defect is formed at the internal interface according to the following reaction:

Case	Dominant defect	Possible oxide formation mechanism
I	$V_O^{z\bullet}$	$\frac{1}{2} O_2 + V_O^{z\bullet} + ze' \leftrightarrow O_O$ $\langle M \rangle \leftrightarrow M_M + V_O^{z\bullet} + ze'$
II	$O_i^{z'}$	$\frac{1}{2} O_2 \leftrightarrow O_i^{z'} + zh^\bullet$ $\langle M \rangle + O_i^{z'} + zh^\bullet \leftrightarrow M_M + O_O$
III	$V_M^{z'}$	$\frac{1}{2} O_2 \leftrightarrow V_M^{z'} + O_O + zh^\bullet$ $\langle M \rangle + V_M^{z'} + zh^\bullet \leftrightarrow M_M$
IV	$M_i^{z\bullet}$	$\frac{1}{2} O_2 + M_i^{z\bullet} + ze' \leftrightarrow M_M + O_O$ $\langle M \rangle \leftrightarrow M_i^{z\bullet} + ze'$

Fig. 1.6. Possible oxidation mechanisms of MO by $V_O^{z\bullet}$, $O_i^{z'}$, $V_M^{z'}$ and $M_i^{z\bullet}$ transport.

This defect diffuses from the internal interface through the metal interstitial sites of the oxide to the external interface. At the external interface, it reacts with oxygen in the atmosphere giving the new construction unit of the oxide according to Reaction 1.25. Fig. 1.16 (case IV) schematises the oxidation mechanism by metal interstitial for the growth of MO.

These four defects ($V_O^{z\bullet}$, $O_i^{z'}$, $V_M^{z'}$ and $M_i^{z\bullet}$) may be categorised as anionic defects ($V_O^{z\bullet}$, $O_i^{z'}$) and cationic defects ($V_M^{z'}$ and $M_i^{z\bullet}$). It is noticed from Fig. 1.16 that if the predominant defect is anionic (cases I and II) it constructs the new unit of oxide at the internal metal/oxide interface, giving the inward growth of the oxide. However, if the dominant defect is cationic (cases III and IV) the new oxide unit is constructed at the external oxide/gas interface, giving the outward growth of the oxide. Furthermore, those defects may be categorised as p-type defects ($O_i^{z'}$ and $V_M^{z'}$) and n-type defect ($V_O^{z\bullet}$ and $M_i^{z\bullet}$) where z is not zero. The p-type defect is created with the formation of electron hole (Eqs. 1.20 and 1.22), while the n-type defect is created with the generation of electron (Eqs. 1.19 and 1.25).

1.4 Phenomenological Oxidation Kinetics

Macroscopically, the oxidation resistance could be assessed by the change of mass per unit area of the sample, a mass gain ($\Delta m/A$), as a function of the oxidation period of time. The relationship between mass gain and oxidation time may be linear, parabolic, linear-parabolic, cubic, logarithmic etc. In the case of linear oxidation kinetics, the relationship between mass gain and the oxidation time is

$$\frac{\Delta m}{A} = k_1 t \quad (1.26)$$

where $\Delta m = m_t - m_{t=0}$ is the change of mass measured at the oxidation time t (m_t) with respect to initial mass before oxidation ($m_{t=0}$), A is the oxidised surface area of the metal and k_1 is the linear rate constant. If the oxidation kinetics is linear, it indicates that the rate determining step of the oxidation is a surface reaction [13]. The example for this is the oxidation of AISI 441 stainless steel oxidised in CO_2 atmosphere as explained in Chapter 6.

In the case of parabolic oxidation kinetics, the relationship between mass gain and time can be expressed by the following relation where k_p is the parabolic rate constant:

$$\left(\frac{\Delta m}{A} \right)^2 = k_p t \quad (1.27)$$

In this case the scale is protective since the increase in mass gain with time ($d(\Delta m/A)/dt$) is reduced at longer periods of oxidation. The parabolic oxidation indicates that the oxide growth is controlled by the diffusion of defect through the oxide scale. Derivation of this rate law based on the diffusion of point defects will be described in Section 1.5.2.

It is noted that the relationships between mass gain and time in Eqs. 1.26 and 1.27 might also be presented as the relationships between the oxide thickness and time. The relation between the oxide thickness (X) and mass gain for the global oxide formation Reaction 1.15 is given in Eq. 1.28.

In this equation, $M_{M_aO_b}$ and M_{O_2} are respectively the molar masses of the oxide M_aO_b and the oxygen gas O_2 , $\rho_{M_aO_b}$ is the density of the oxide, A is the oxidised surface area of the sample, and Δm_{O_2} is the mass of oxygen gas consumed to form the oxide which is in fact equal to the increase of mass that is measured from the experiment (Δm). The relation in Eq. 1.28 was derived using the stoichiometric relations in the oxidation Reaction 1.15 and the relation $\rho_{M_aO_b} = (\Delta m_{M_aO_b} / \Delta V) = (\Delta m_{M_aO_b} / AX)$ where $\Delta m_{M_aO_b}$ is mass of the oxide formed during oxidation.

$$X = \frac{2}{b} \left(\frac{M_{M_aO_b}}{M_{O_2}} \right) \frac{1}{\rho_{M_aO_b}} \left(\frac{\Delta m}{A} \right) \quad (1.28)$$

Furthermore, it is often found from the experiment that the rate constant (k) relates with temperature in the following Arrhenius form:

$$k = k^\circ \exp\left(\frac{-E_a}{RT}\right) \quad (1.29)$$

Here k° is the pre-exponential factor having the same unit as k , E_a the apparent activation energy, R the gas constant, and T the absolute temperature. Eq. 1.29 can also be written as shown in Eq. 1.30. This relation indicates that the Arrhenius relation between the logarithm of k_p and the reciprocal temperature is linear.

$$\log k = \left(-\frac{E_a}{10^4 (\ln 10) R} \right) \cdot \frac{10^4}{T} + \log k^\circ \quad (1.30)$$

As explained by Kofstad [22], when the reaction proceeds, a transition state is assumed to exist at the top of the free energy barrier separating the initial and the final states. It is considered that the species in the transition and the initial states are in equilibrium and the activation energy E_a is the height of the free energy barrier [22]. The change in the activation energy may suggest the possible change in the rate determining step of the oxidation reaction [13, 22].

Fig. 1.7(a) exemplifies the oxidation results of the iron oxidised in oxygen at the 700–900 °C [23]. The value of mass gain is squared and plotted as a function of time as shown in Fig. 1.7(b). The linear relationship of the plot between square of mass gain and time exhibits the parabolic oxidation kinetics, and the slope of this plot is the value of the parabolic rate constant. Fig. 1.7(c) shows the logarithm of k_p as a function of the reciprocal temperature. The linear relation in this plot was obtained with the R^2 of 0.997. This means that the oxidation of iron follows the Arrhenius relation with the apparent activation energy, which was extracted from slope of the line in Fig. 1.7(c), of 141 kJ mol⁻¹.

Fig. 1.8 shows the Arrhenius relation of different oxides [23–25]. It is seen that the parabolic rate constants of alumina and chromia are significantly lower than the rate of the formation of iron oxides on iron. For example, at 1000 °C, the parabolic rate constant for the formation of iron oxides is about 10⁻⁶ g² cm⁻⁴ s⁻¹. This value is lower to be about 10^{-10.5} to 10⁻¹² g² cm⁻⁴ s⁻¹ for the chromia formation, such as 2 × 10⁻¹¹ g² cm⁻⁴ s⁻¹ (10^{-10.70} g² cm⁻⁴ s⁻¹) for the growth of chromia on Fe–20Cr [13]. It is even lower to about 10^{-12.2} to 10⁻¹³ g² cm⁻⁴ s⁻¹ for the alumina formation, such as 2.7 × 10⁻¹³ g² cm⁻⁴ s⁻¹ (10^{-12.57} g² cm⁻⁴ s⁻¹) for the growth of alumina on Fe–25Cr–5Al [13]. These results indicate the effectiveness of the chromia and alumina scale to combat the high temperature corrosion of metals.

Fig. 1.7. (a) Mass gain as a function time, (b) square of mass gain as a function of time, and (c) the Arrhenius relation of the iron oxidised in oxygen at 700–900 °C. Redrawn and adapted from S. Chandra-ambhorn et al., Corros. Sci. 148 (2019) 355–365 [23].

Fig. 1.8. Arrhenius plot for the formation of different oxides [23–25].

1.5 Derivation of the Parabolic Rate Law

1.5.1 Fick's First Law for the Diffusion of Defect through the Oxide

To derive the parabolic rate law, we start from the uni-directional phenomenological Fick's first law as follows [26, 27]:

$$\bar{j}_{\delta} = -D_{\delta} \frac{\partial C_{\delta}}{\partial x} \bar{u}_x \quad (1.31)$$

Here, $\bar{j}_{\delta}$ is the molar flux of a species δ ($\text{mol cm}^{-2} \text{s}^{-1}$), D_{δ} the diffusivity of the species δ ($\text{cm}^2 \text{s}^{-1}$), C_{δ} the concentration of the species δ (mol cm^{-3}), and $\bar{u}_x$ the unit vector in x direction. The generalised Fick's first law [13, 26] is

$$\bar{j}_{\delta} = -\frac{D_{\delta} C_{\delta}}{RT} \frac{\partial \tilde{\mu}_{\delta}}{\partial x} \bar{u}_x \quad (1.32)$$

where $\tilde{\mu}_{\delta}$ is the electrochemical potential of the species δ which might be charged. It relates to the chemical potential of the species δ (μ_{δ}) as follows [13]:

$$\tilde{\mu}_{\delta} = \mu_{\delta} \pm z_{\delta} F \phi \quad (1.33)$$

where

$$\mu_{\delta} = \mu_{\delta}^{\circ} + RT \ln a_{\delta} \quad (1.34)$$

Here, z_{δ} is a degree of ionisation of the species δ , F the Faraday's constant (96485 C mol^{-1}) [28], ϕ the electric potential at the coordinate x (V), μ_{δ}° the chemical potential of the species δ at

standard state (J), and a_δ the activity of the species δ . The positive (negative) sign is used in the right-hand side of Eq. 1.33 if the electric charge of the species δ is positive (negative).

By assuming that the activity of δ equals its concentration C_δ in the unit of mol cm^{-3} relative to the concentration at standard state i.e. 1 mol cm^{-3} , it can be written that

$$\mu_\delta = \mu_\delta^\circ + RT \ln C_\delta \quad \text{or} \quad (1.35)$$

$$d\mu_\delta = RT d \ln C_\delta = \frac{RT}{C_\delta} dC_\delta \quad (1.36)$$

It is noticed that for the electrically neutral species A, $\tilde{\mu}_\delta = \mu_\delta$. From that relation and Eq. 1.36 we can obtain that $d\tilde{\mu}_\delta = d\mu_\delta = (RT/C_\delta)dC_\delta$. In this case, the generalised Fick's first law in Eq. 1.32 can be reduced to be the phenomenological one in Eq. 1.31.

It is also noted that the molar concentration (C_δ) in the unit of mol cm^{-3} relates to the mole fraction of the species δ ($[\delta]$) according to Eq. 1.37 where Ω is the molar volume ($\text{cm}^3 \text{ mol}^{-1}$) of the interested solution:

$$C_\delta = \frac{[\delta]}{\Omega} \quad (1.37)$$

Furthermore, the rate of the construction of M_aO_b per unit area ($r_{\text{M}_a\text{O}_b}$), in the unit of $\text{mol cm}^{-2} \text{ s}^{-1}$, can be written as a function of the rate of increase in oxide thickness (X) as follows [13]:

$$r_{\text{M}_a\text{O}_b} = \frac{1}{\Omega} \frac{dX}{dt} \quad (1.38)$$

In the diffusion of point defects, the species δ may be charged and as a result affected by the applied electric field. To understand the phenomena, let consider the case when $\partial\mu_\delta/\partial x = 0$ and a positively charged species of 1 Coulomb is transported with the velocity of $\bar{v}$ along the direction of the electric field $\bar{E}$. Electric field ($\bar{E}$) is defined as a force applied on a positive charge per its charge (N C^{-1}) and equals the negative gradient of the electric potential ϕ (V m^{-1}) in the following form [29]:

$$\bar{E} = -\frac{\partial\phi}{\partial x} \bar{u}_x \quad (1.39)$$

If it is supposed that the movement of this charged species causes the friction force exerted on it to be proportional to the velocity of the charged species, such friction force is therefore equal to $-k_\delta \bar{v}_\delta$ where k_δ is a constant of proportionality [26]. The stationary limiting velocity is attained when this friction force is balanced by $\bar{E}$ which in this case is the force applied by the electric field, i.e. $\bar{E} = k_\delta \bar{v}_\delta$ [26]. This relation may be expressed in general as in Eq. 1.40 where U_δ equals $(1/k_\delta)$ and called the electrical mobility in the unit of $\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The positive (negative) sign is used in the right-hand side of Eq. 1.40 when the charge of the species δ is positive (negative) [30].

$$\bar{v}_\delta = \pm U_\delta \bar{E} \quad (1.40)$$

Electrical mobility of the charged species contributes to many properties of materials, including the electrical conductivity (σ) of material. The relationship between the electrical mobility and conductivity can be obtained, starting from the following Faraday's law for the migration of the charged species under the pure electric field [26]:

$$\vec{i}_\delta = z_\delta F \vec{j}_\delta \quad (1.41)$$

Consider the case where the positively charged species with the molar flux of $\vec{j}_\delta$ passes perpendicularly to the area A along the length dl , causing the current density of $\vec{i}_\delta$. The Ohm's law states that $I_\delta = \Delta\phi / R_\delta$ where I_δ is the electric current, $\Delta\phi$ is the potential difference between two terminals of interest, and R_δ is the electrical resistance of the interested part. By inserting the terms $I_\delta = \int \vec{i}_\delta \cdot d\vec{A}$ and $\Delta\phi = \int \vec{E} \cdot d\vec{l}$ and $R = dl / (\sigma \cdot dA)$ into the Ohm's law and by taking into account the fact that the directions of $d\vec{A}$, $d\vec{l}$ and $\vec{E}$ are the same, it can be obtained that [26, 29]

$$\vec{i}_\delta = \pm \sigma \vec{E} \quad (1.42)$$

where the positive (negative) sign is used in the right-hand side of this equation when the charge of the interested species is positive (negative).

Furthermore, in the case that $\partial\mu_\delta / \partial x = 0$, the molar flux of the species δ can also be written as [26]

$$\vec{j}_\delta = C_\delta \vec{v}_\delta = \pm C_\delta U_\delta \vec{E} \quad (1.43)$$

By inserting Eqs. 1.42 and 1.43 into Eq. 1.41, it can be obtained that

$$\sigma_\delta = z_\delta F C_\delta U_\delta \quad (1.44)$$

This equation expresses the relationship between the electrical mobility and conductivity. It will be used to compare the electrical conductivities of the charged species during oxide growth in the derivation of the parabolic rate law in Section 1.5.2.

Furthermore, in the case that $\partial\mu_\delta / \partial x = 0$, from Eqs. 1.32, 1.33 and 1.39, the molar flux of the species δ can be written in the following form:

$$\vec{j}_\delta = \pm z_\delta F \frac{D_\delta C_\delta}{RT} \vec{E} \quad (1.45)$$

From Eqs. 1.43 and 1.45, the following relation can be obtained:

$$U_\delta = \frac{z_\delta F}{RT} D_\delta \quad (1.46)$$

From Eqs. 1.32–1.34, 1.37 and 1.46, we can obtain

$$\vec{j}_\delta = -\frac{1}{\Omega} (D_\delta \frac{\partial[\delta]}{\partial x} \pm U_\delta [\delta] \frac{\partial\phi}{\partial x}) \vec{u}_x \quad (1.47)$$

The Fick's first law in this form will be used to derive the parabolic rate law as the following.

1.5.2 Parabolic Rate Law

In this section, we will derive the relationship between k_p with the defect concentration and oxygen partial pressure, starting from the case that the oxide M_aO_b is p-type with a dominant metal vacancy and a dominant electronic conductivity [13]. In such case, the relationship of the point defect with electron hole and oxygen partial pressure is shown in Reaction 1.22. From Eq. 1.47, the molar fluxes of metal vacancy and electron hole can be written as follows:

$$\bar{j}_{V_M^{z'}} = -\frac{1}{\Omega} (D_{V_M^{z'}} \frac{\partial [V_M^{z'}]}{\partial x} - U_{V_M^{z'}} [V_M^{z'}] \frac{\partial \phi}{\partial x}) \bar{u}_x \quad (1.48)$$

$$\bar{j}_{h^\bullet} = -\frac{1}{\Omega} (D_{h^\bullet} \frac{\partial [h^\bullet]}{\partial x} + U_{h^\bullet} [h^\bullet] \frac{\partial \phi}{\partial x}) \bar{u}_x \quad (1.49)$$

with the electroneutrality condition of

$$z[V_M^{z'}] = [h^\bullet] \quad (1.50)$$

By eliminating $\partial \phi / \partial x$ using Eqs. 1.48 and 1.49, then replacing the electron hole concentration with metal vacancy one using Eq. 1.50, and changing the constant (RT/zF) to $D_{V_M^{z'}}/U_{V_M^{z'}}$ using Eq. 1.46, we obtain

$$\frac{\bar{j}_{V_M^{z'}}}{U_{V_M^{z'}} [V_M^{z'}]} + \frac{\bar{j}_{h^\bullet}}{U_{h^\bullet} [h^\bullet]} = -\frac{(z+1)D_{V_M^{z'}}}{\Omega U_{V_M^{z'}}} \frac{\partial \ln[V_M^{z'}]}{\partial x} \bar{u}_x \quad (1.51)$$

In the case that the electrical conductivity of electronic defect i.e. electron hole is significantly higher than that of the ionic defect i.e. metal vacancy, from Eq. 1.44 we may write that

$$U_{h^\bullet} [h^\bullet] \gg U_{V_M^{z'}} [V_M^{z'}] \quad (1.52)$$

From the relationship in Eq. 1.52, Eq. 1.51 can be simplified to be the following expression:

$$\bar{j}_{V_M^{z'}} = -\frac{1}{\Omega} (z+1) D_{V_M^{z'}} \frac{\partial [V_M^{z'}]}{\partial x} \bar{u}_x \quad (1.53)$$

From this equation it can be seen that if the diffusing species is not charged ($z=0$), Eq. 1.53 is simply the Fick's first law. However, if the diffusing species is charged with the degree of ionisation of z , the molar flux will be increased by the factor of $(z+1)$. This equation can be integrated as shown in Eq. 1.54 from the position at the external interface ($x=0$) where the metal vacancy concentration is $[V_M^{z'}]_e$ to the position at the internal interface, i.e. at the position X corresponding to the value of the oxide thickness, where the metal vacancy concentration is $[V_M^{z'}]_i$.

$$\int_{[V_M^{z'}]_e}^{[V_M^{z'}]_i} d[V_M^{z'}] \bar{u}_x = \int_0^X \frac{-\Omega \cdot \bar{j}_{V_M^{z'}}}{(z+1) D_{V_M^{z'}}} dx \quad (1.54)$$

If it is assumed that the flux and diffusivity in equation are constant throughout the oxide, it can be obtained that

$$\bar{j}_{V_M^{z'}} = \frac{1}{\Omega} (z+1) D_{V_M^{z'}} \left(\frac{[V_M^{z'}]_e - [V_M^{z'}]_i}{X} \right) \bar{u}_x \quad (1.55)$$

From Eqs. 1.38, 1.55 and the stoichiometric relation between M and M_aO_b in the oxide formation, we can obtain that

$$X^2 = k'_p t \quad (1.56)$$

where

$$k'_p = \frac{2}{a} (z+1) D_{V_M^{z'}} ([V_M^{z'}]_e - [V_M^{z'}]_i) \quad (1.57)$$

Here k'_p is the parabolic rate constant from the relation between the oxide thickness and time. By inserting X from Eq. 1.28 into Eq. 1.56, we can obtain the relationship between mass gain and the oxidation time in the form of Eq. 1.27 with the parabolic rate constant (k_p) of

$$k_p = \frac{b^2}{2a} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{V_M^{z'}} ([V_M^{z'}]_e - [V_M^{z'}]_i) \quad (1.58)$$

From the equilibrium constant of Eq. 1.22 and the electroneutrality condition in Eq. 1.50, it can be obtained that

$$[V_M^{z'}] = \left(\frac{K_{1.22}}{z^{az}} \right)^{\frac{1}{a(z+1)}} \frac{b}{p_{O_2}^{2a(z+1)}} \quad (1.59)$$

It is noted that in the case of chromia (Cr_2O_3) thermally grown on chromium in air, the oxygen partial pressure at the external interface ($p_{O_2,e}$) is 0.21 bar while that pressure at the internal chromium/chromia interface ($p_{O_2,i}$) is drastically lower i.e. about 5×10^{-28} bar at 800 °C [15]. If the oxygen partial pressure at the external interface is drastically higher than that at the internal one, the metal vacancy at the external interface is also tremendously higher than that at the internal interface. In such case Eq. 1.58 can be reduced to be

$$k_p = \frac{b^2}{2a} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{V_M^{z'}} [V_M^{z'}]_e \quad (1.60)$$

From Eqs. 1.59 and 1.60, we can obtain that

$$k_p = \left(\frac{K_{1.22}}{z^{az}} \right)^{\frac{1}{a(z+1)}} \frac{b^2}{2a} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{V_M^{z'}} p_{O_2,e}^{\frac{b}{2a(z+1)}} \quad (1.61)$$

Eqs. 1.60 and 1.61 express that the parabolic rate constant depends on many factors particularly the oxygen partial pressure at the external interface which prescribes the metal vacancy

concentration there. It depends on the diffusivity of metal vacancy in the oxide and the degree of ionisation of the defect. Also, it also depends on the molar mass and density of the oxide as well as a and b which represent the stoichiometric proportion between metal and oxygen in the oxide.

In the case of another p-type M_aO_b with a dominant oxygen interstitial and a dominant electronic conductivity, k_p can be obtained in the form shown in Eq. 1.62. It is still observed that the k_p also depends on the oxygen partial pressure but with the exponent of $1/2(z+1)$.

$$k_p = \left(\frac{K_{1.20}^{1/b}}{Z^z} \right)^{\frac{1}{z+1}} \frac{b}{2} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{O_i^{z\bullet}} \frac{1}{p_{O_{2,e}}^{2(z+1)}} \quad (1.62)$$

For the n-type M_aO_b which has oxygen vacancy as a dominant defect and also has a dominant electronic conductivity, we can derive in the similar manner as the case of metal vacancy to obtain the parabolic relation between mass gain and time in the form of Eq. 1.27. However, the rate constant in this case is

$$k_p = \frac{b}{2} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{V_O^{z\bullet}} ([V_O^{z\bullet}]_i - [V_O^{z\bullet}]_e) \quad (1.63)$$

From the equilibrium constant of Eq. 1.19 and the electroneutrality condition i.e. $[e'] = z[V_O^{z\bullet}]$, it can be obtained that

$$[V_O^{z\bullet}] = \left(\frac{1}{K_{1.19}^{1/b} Z^z} \right)^{1/(z+1)} \cdot \frac{1}{p_{O_2}^{1/2(z+1)}} \quad (1.64)$$

In the case of chromia thermally grown on chromium in air at 800 °C, the p_{O_2} in equilibrium between chromium and chromia is about 5×10^{-28} bar as previously mentioned. This value is drastically lower than the oxygen partial pressure at the external interface which is 0.21 bar. Thus, $1/p_{O_{2,i}}^{1/2(z+1)}$ is drastically higher than $1/p_{O_{2,e}}^{1/2(z+1)}$, and as a consequence the oxygen vacancy concentration at the internal interface is also tremendously higher than that at the internal interface. In such case Eq. 1.63 can be reduced to be

$$k_p = \frac{b}{2} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{V_O^{z\bullet}} [V_O^{z\bullet}]_i \quad (1.65)$$

From Eqs. 1.64 and 1.65, we can obtain that

$$k_p = \left(\frac{1}{K_{1.19}^{1/b} Z^z} \right)^{1/(z+1)} \frac{b}{2} \left(\frac{M_{O_2}}{M_{M_aO_b}} \right)^2 \rho_{M_aO_b}^2 (z+1) D_{V_O^{z\bullet}} \frac{1}{p_{O_{2,i}}^{1/2(z+1)}} \quad (1.66)$$

In the case of the n-type oxide with a dominant metal interstitial and a dominant electronic conductivity, k_p can also be obtained as follows:

$$k_p = \left(\frac{1}{K_{1.25} z^{az}} \right)^{1/a(z+1)} \frac{b^2}{2a} \left(\frac{M_{O_2}}{M_{M_a O_b}} \right)^2 \rho_{M_a O_b}^2 (z+1) D_{M_i^{z\bullet}} \frac{1}{p_{O_2,i}^{b/2a(z+1)}} \quad (1.67)$$

It can be seen that the k_p of the n-type oxide growth according to Eqs. 1.66 and 1.67 are independent of the oxygen partial pressure at the external interface, while the k_p of the p-type oxide growth according to Eqs. 1.61 and 1.62 depend on the oxygen partial pressure in the atmosphere. Thus the variation of the k_p with the oxygen partial pressure in the atmosphere can be used to identify if the dominant defect responsible for the growth is p-type (i.e. $V_M^{z'}$ or $O_i^{z'}$) or n-type (i.e. $V_O^{z\bullet}$ and $M_i^{z\bullet}$). For the p-type defect, we can further identify the dominant defect as an anionic defect ($O_i^{z'}$) if the oxide growth is inward and as a cationic defect ($V_M^{z'}$) if the oxide growth is outward. The same consideration can be done for the case of the n-type defects. By this way, the dominant defect responsible for the oxide growth can be identified.

1.6 Summary

This chapter introduces the classification of stainless steels for the high temperature applications. The guidance of the maximum isothermal service temperature of some important stainless steels is given. Thermodynamic concept is further explained in order to give the framework for predicting the stable phases in the studied condition. Example of the thermodynamic analysis of the formation of thermal oxide on stainless steel is given. Further, types of defect in the oxide and the Fick's first law for the diffusion of defect through the oxide are explained. The oxidation kinetics is reviewed starting from the phenomenological laws of linear and parabolic reaction rate as well as the Arrhenius relation. The derivation of the parabolic rate law is given especially for the case that the oxide is p-type with a dominant metal vacancy and a dominant electronic conductivity.

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