

CHAPTER 4

High Temperature Oxidation of Stainless Steels

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Abstract. This chapter is dedicated to the description of high temperature oxidation of both chromia and alumina forming alloys. The defect structures of iron and chromium are firstly reviewed. The effects of elements on stainless steel oxidation behaviour are further addressed. For the chromia-forming stainless steel, the oxidation rate is reduced with the increased silicon content but not in a monotonic manner. Titanium and niobium can reduce breakaway oxidation of Fe–18Cr–10Ni austenitic stainless steel. Titanium can enhance the adhesion of scale to the Fe–18Cr by mechanical keying effect of TiO₂ formed at the steel/scale interface. For the alumina-forming stainless steel, the formation of alumina and its transformation during oxidation are reviewed. Chromium can be added to reduce the critical aluminium content in the steels in order to form alumina at high temperatures. The addition of reactive elements with appropriate level can improve scale adhesion and reduce the steel oxidation rate. Refractory element like molybdenum can increase strength of material but also accelerate the oxidation rate of the steels containing reactive elements. The development of new alumina-forming austenitic alloy grades is finally described.

4.1 Oxidation of Iron and Chromium

4.1.1 Oxidation Mechanism of Iron

The formation of thermal oxide on pure iron is well known, although complex, and is briefly described in this section. At temperatures higher than the eutectoid temperature of the Fe–O system i.e. 570 °C, the formed thermal oxide scale typically consists of the thickest wüstite, with magnetite sitting on the wüstite layer and the outermost haematite sitting on magnetite [1]. Païdassi [2, 3] reported that, for the iron oxides grown at 700–1250 °C in air, haematite was about 1% while magnetite was about 3.5–5 % thick. It was reported that the predominant defects in wüstite and magnetite are iron vacancy, while the dominant defect in haematite is oxygen vacancy [4]. Based on this defect structure, the growth mechanism of iron oxides on iron may be described [4] as shown in Fig. 3.1.

For the growth of haematite, at the scale/gas interface oxygen adsorbs on the solid surface i.e.



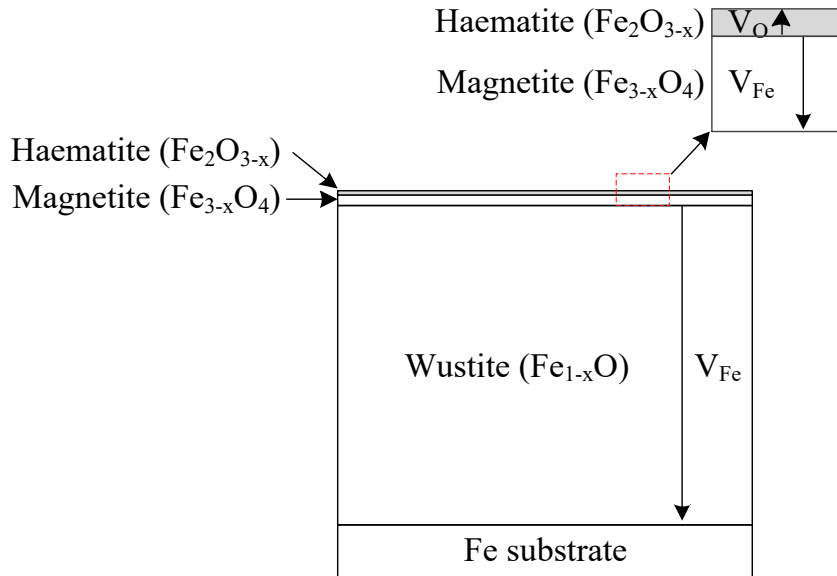


Fig. 4.1. Typical thermal oxide scale on iron at 900 °C in air with the proportion of oxide phases according to Païdassi [2, 3] and with dominant defects in each oxide according to Sarrazin et al. [4].

where s is the available site on the surface and $O-s$ is the adsorbed oxygen on the surface. At the interface between magnetite and haematite, the oxygen vacancy is created by the following reaction:



Subscripts h, m, w indicate that the considered entity is in haematite, magnetite and wüstite phase respectively. The formed oxygen vacancy according to Reaction 4.2 diffuses outwards to the haematite/gas interface. At that interface, the adsorbed oxygen according to Reaction 4.1 jumps into the oxygen vacancy in the haematite according to the following reaction:



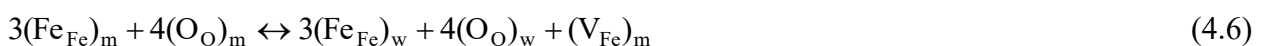
For the growth of magnetite, at the magnetite/haematite interface, oxygen on the oxygen site in haematite $((\text{O}_{\text{O}})_{\text{h}})$ is used to form the new magnetite unit. However, because the iron activity at this interface is lower than that at the wüstite/magnetite interface, the iron vacancy can then be formed as follows:



The formed iron vacancy diffuses to the wüstite/magnetite interface. At that interface, iron on the normal iron site in wüstite $((\text{Fe}_{\text{Fe}})_{\text{w}})$ jumps into the metal vacancy in magnetite according to the following reaction:



For the growth of wüstite, at the wüstite/magnetite interface, one unit of magnetite is used to construct the new wüstite unit. Because the ratio of oxygen and iron in magnetite is higher than that in wüstite, the formation of wüstite from magnetite then gives iron vacancy as follows:



The formed iron vacancy in wüstite ($(V_{Fe})_w$) diffuses towards the wüstite/iron interface. At that interface, iron in the matrix, $\langle Fe \rangle$, jumps into the iron vacancy in wüstite according to the reaction:



It is noted that at the temperature of 570 °C, there exists the eutectoid reaction among wüstite, iron and magnetite. Thus when wüstite is cooled down from high temperatures to 570 °C or lower temperatures, wüstite can decompose giving the eutectoid structure consisting of iron and magnetite, as typically observed in the thermal oxide on hot-rolled low carbon steel where the cooling rate of the strip is essentially slow [1, 5–7].

4.1.2 Oxidation Mechanism of Chromium

Latu-Romain et al. [8–10] have reported that the chromia thermally grown on chromium consists of the columnar external part and the equiaxed internal one. It is proposed that the dominant defect in the external chromia is the p-type chromium vacancy, while the dominant defect in the internal chromia is the n-type oxygen vacancy as sketched in Fig. 4.2, when the external oxygen partial pressure is superior or equal to 10^{-12} atm.

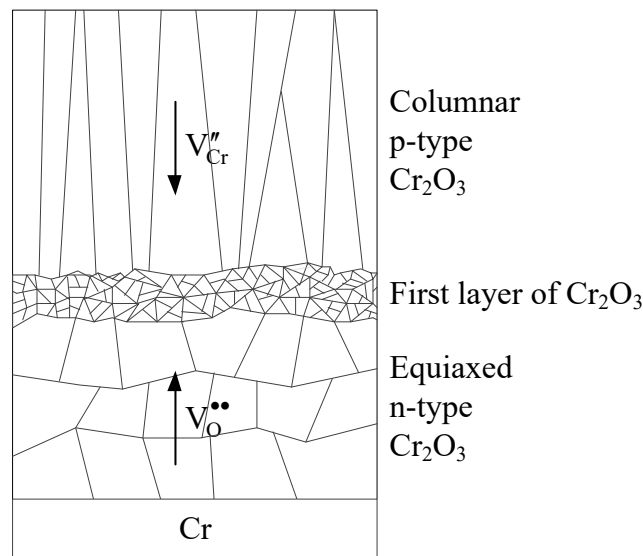


Fig. 4.2. Structure of chromia thermally grown on chromium. Redrawn and adapted from L. Latu-Romain et al., *Oxid. Met.* 86 (2016) 497–509 [8].

As suggested by Latu-Romain et al. [8], the defect concentrations in chromia can be analysed as a function of the oxygen partial pressure, giving the Brouwer diagram, as follows.

The relevant defect reactions are



with the equilibrium constants of

$$K_{4.8} = \frac{[V_{Cr}''']^2 [h^\bullet]^6}{p_{O_2}^{3/2}} \quad (4.12)$$

$$K_{4.9} = \frac{1}{p_{O_2}^{3/2} [V_O^{\bullet\bullet}]^3 [e']^6} \quad (4.13)$$

$$K_S = [V_{Cr}''']^2 [V_O^{\bullet\bullet}]^3 \quad (4.14)$$

$$K_e = [e'] [h^\bullet] \quad (4.15)$$

$K_{4.8}$ and $K_{4.9}$ are equilibrium constants of Reactions 4.8 and 4.9 respectively. K_S and K_e are equilibrium constants of Schottky defect reaction i.e. Reaction 4.10, and Reaction 4.11 respectively. The electroneutrality condition for this problem is

$$2[V_O^{\bullet\bullet}] + [h^\bullet] = 3[V_{Cr}'''] + [e'] \quad (4.16)$$

The dominant regimes of defects may be considered as follows.

Regime I is the case at relatively low p_{O_2} where oxygen vacancy and electron are dominant as can be seen from Reaction 4.9. In this case the electroneutrality condition described in Eq. 4.16 can be reduced to the following one:

$$2[V_O^{\bullet\bullet}] = [e'] \quad (4.17)$$

Regime II is the case at intermediate p_{O_2} . By considering that the electronic defect was dominant in this regime [8], the following electroneutrality condition can be drawn:

$$[e'] = [h^\bullet] \quad (4.18)$$

Regime III is the case at relatively high p_{O_2} where metal vacancy and electron hole are dominant as suggested by Reaction 4.8. In this case the electroneutrality condition described in Eq. 4.16 can be reduced to the following one:

$$[h^\bullet] = 3[V_{Cr}'''] \quad (4.19)$$

As for Regime I, from Eqs. 4.13 and 4.17, the oxygen vacancy concentration can be expressed in the following form:

$$[V_O^{\bullet\bullet}] = 2^{-2/3} K_{4.9}^{-1/9} p_{O_2}^{-1/6} \quad (4.20)$$

From Eq. 4.20 and the electroneutrality condition according to Eq. 4.17, it can be obtained that

$$[e'] = 2[V_O^{\bullet\bullet}] = 2^{1/3} K_{4.9}^{-1/9} p_{O_2}^{-1/6} \quad (4.21)$$

From Eq. 4.21 and electronic defect equilibrium constant in Eq. 4.15, we obtain that

$$[h^\bullet] = 2^{-1/3} K_e K_{4.9}^{1/9} p_{O_2}^{1/6} \quad (4.22)$$

From Eq. 4.20 and the Schottky defect equilibrium constant in Eq. 4.14, the chromium vacancy concentration can be obtained as follows:

$$[V_{Cr}'''] = 2 K_{4.9}^{1/6} K_S^{1/2} p_{O_2}^{1/4} \quad (4.23)$$

For Regime II, from Eq. 4.15 and the electroneutrality condition in Eq. 4.18, we obtain that

$$[e'] = [h^\bullet] = K_e^{1/2} = \text{constant} \quad (4.24)$$

Inserting Eq. 4.24 into Eq. 4.12 gives

$$[V_{Cr}'''] = K_{4.8}^{1/2} K_e^{-3/2} p_{O_2}^{3/4} \quad (4.25)$$

Inserting Eq. 4.24 into Eq. 4.13 gives

$$[V_O^{\bullet\bullet}] = K_{4.9}^{-1/3} K_e^{-1} p_{O_2}^{-1/2} \quad (4.26)$$

For Regime III, by inserting the electroneutrality condition according to Eq. 4.19 into Eq. 4.12, the chromium vacancy concentration can be obtained in the following form:

$$[V_{Cr}'''] = 3^{-3/4} K_{4.8}^{1/8} p_{O_2}^{3/16} \quad (4.27)$$

From Eq. 4.27 and electroneutrality condition according to Eq. 4.19, we obtain that

$$[h^\bullet] = 3[V_{Cr}'''] = 3^{1/4} K_{4.8}^{1/8} p_{O_2}^{3/16} \quad (4.28)$$

From Eqs. 4.28 and 4.15, it can be obtained that

$$[e'] = 3^{-1/4} K_e K_{4.8}^{-1/8} p_{O_2}^{-3/16} \quad (4.29)$$

From Eq. 4.27 and the Schottky defect equilibrium constant in Eq. 4.14, the oxygen vacancy concentration can be expressed in the following form:

$$[V_O^{\bullet\bullet}] = 3^{1/2} K_S^{1/3} K_{4.8}^{-1/12} p_{O_2}^{-1/8} \quad (4.30)$$

By using Eqs. 4.20–4.30, the Brouwer diagram of the chromia thermally grown on chromium in oxygen can be drawn as shown in Fig. 4.3. It was reported [9] that the transition zone between the high p_{O_2} region where metal vacancy is dominant and the intermediate p_{O_2} region was reported to be in the p_{O_2} range of 5×10^{-13} to 10^{-12} atm. The transition zone between the low p_{O_2} region where oxygen vacancy is dominant and the intermediate one was reported to be in the p_{O_2} range of 10^{-14} to 5×10^{-14} atm [9].

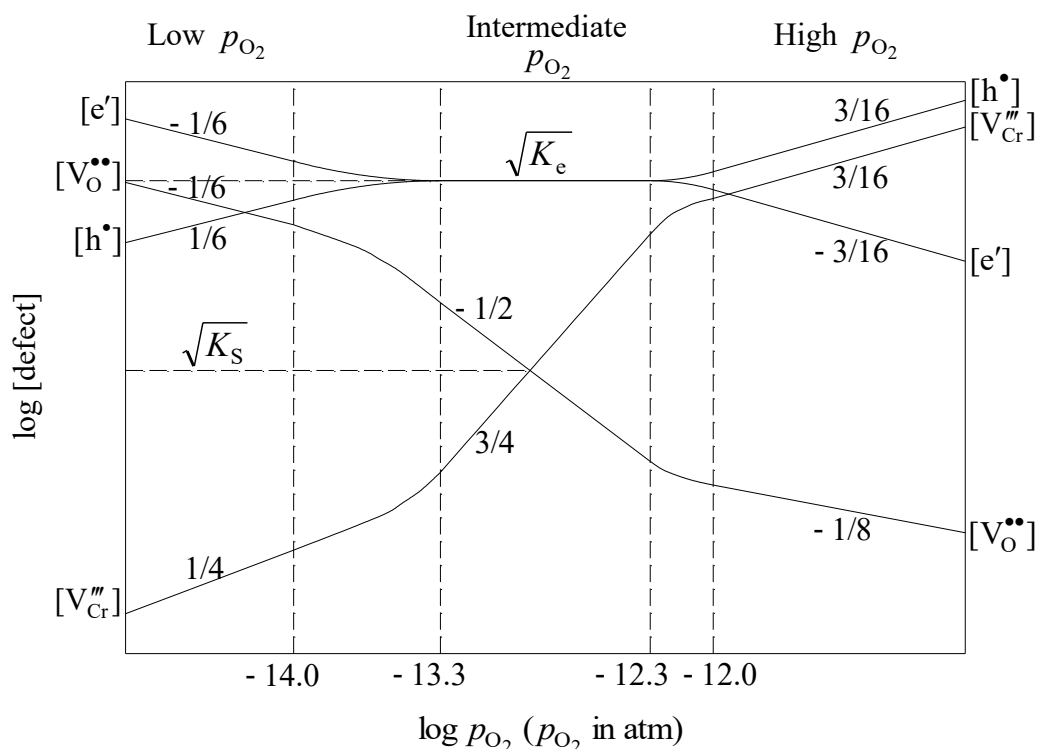


Fig. 4.3. Brouwer diagram of chromia thermally grown on chromium in oxygen. Redrawn and adapted from L. Latu-Romain et al., *Oxid. Met.* 86 (2016) 497–509 [8], L. Latu-Romain et al., *Corros. Sci.*, 141 (2018) 46–52 [9] and L. Latu-Romain et al., *Corros. Sci.* 126 (2017) 238–246 [10].

4.2 Chromia-Forming Stainless Steel

For the Fe–2.25Cr steel (unless stated otherwise, the alloy composition is in wt.%), it was reported that after oxidation in dry air at 600 °C, the oxide formed on this steel was poorly protective and comprised haematite sitting on magnetite and Fe–Cr spinel [11]. When chromium increases up to 18 wt.%, the chromia topped with Cr–Mn spinel can be formed as previously shown and discussed in Fig. 1.4. In the case that other alloying elements are added to the steel, they may form the oxide as layer or nodule and affect properties of the scale as will be reviewed in the following.

4.2.1 Effect of Silicon

In the case of carbon steel, Chandra-ambhorn et al. [12] oxidised iron with silicon contents of 0.23 and 1.03 wt.% in Ar–20% H₂O. It was found that the oxidation rate was linear-parabolic. The addition of silicon to the steel formed fayalite (Fe₂SiO₄) as an intermediate layer between substrate and iron oxides. It was reported that diffusivity of iron in fayalite is slower than that in wüstite [12, 13]. As a result, the formation of this layer could reduce the steel oxidation rate by inhibiting the outward diffusion of iron from the substrate to form iron oxides. However, the scale of steel with 1.03 wt.% of silicon was found to be thicker than that of the steel with 0.23 wt.% of silicon. To explain this result, even though the external iron oxides of the former steel was thinner than that of the later steel, the internal fayalite layer of the former steel was thicker in higher degree thus resulting in increasing the total scale thickness. In the case of stainless steel, Bamba et al. [14] studied the oxidation of Fe–15Cr without and with 0.5 and 1 wt.% of silicon. It was found that increasing silicon content could reduce the steel oxidation rate but the oxidation rate of Fe–15Cr–0.5Si was slower than that of Fe–15Cr–1Si. The discontinuous silica precipitates was found at the metal/scale interface and beneath the oxide scale for the oxidised Fe–15Cr–0.5Si, while the

continuous silica layer was found at the interface between the chromia scale and the Fe–15Cr–1Si substrate. They proposed that the most reduced oxidation rate of the Fe–15Cr–0.5Si is not from the formation of silica as a barrier to prevent the incorporation of chromium into the oxide scale but probably from the formation of silica precipitates which inhibits the diffusion of chromium from steel to the metal/scale interface by providing sinks for the injected metal vacancies [14]. If chromium vacancy is inhibited to enter the metal, it can be accumulated at the scale/steel interface and as a result reduces the scale adhesion as observed in that work [14].

4.2.2 Effects of Titanium and Niobium

Wongpromrat et al. [15] studied the formation of titanium and niobium rich oxide on Fe–18Cr–0.13Ti–0.55Nb (AISI 441) oxidised at 800 °C in O₂-5% H₂O for 24 h. It was found that the oxide nodule could be formed above Fe₂Nb which was precipitated at the metal grain boundary. This Fe–Nb intermetallic compound appears in the Fe–Nb system during tempering operations [15,16]. The nodule could also be formed at the heart of the grain as shown in Fig. 4.4. From this figure, we can see the thin continuous chromia layer outside the nodule. However, in fact this layer also lies at the middle of the nodule indicating the original formation of the chromia layer in that area. Titanium can diffuse to the chromia layer and dissolves there. It can also transport to the top surface to form titania. Niobium is found to accompany titanium and can dissolve in titania. Fig. 4.4 and the Raman spectroscopy results reported in literature [15] indicated that the nodule external part consists mainly of Ti(Nb)O₂. Fig. 4.5 shows the three dimensional image of the oxide nodule above the grain of AISI 441 after oxidation at 800 °C in O₂-5% H₂O for 24 h. We can see that the nodule is connected to the surrounding scale and situates above the intragranular niobium-rich precipitates. The size of precipitate tends to be smaller when it is closer to the nodule, suggesting that the nodule growth is a driving force for the precipitate dissolution and the transport of titanium and niobium to the nodule. This precipitate could correspond to NbC and/or (Ti, Nb)(C, N) [15,16].

The addition of titanium and niobium can also affect properties of both metal and oxide scale formed at high temperatures. Toscan et al. [17] studied the oxidation of ferritic stainless steels (Fe–18Cr, Fe–18Cr–0.41Ti, Fe–18Cr–0.58Nb) and austenitic ones (Fe–18Cr–10Ni, Fe–18Cr–10Ni–0.32Ti, Fe–18Cr–10Ni–0.46Nb) at 950 °C in laboratory air. The results are shown in Fig. 4.6.

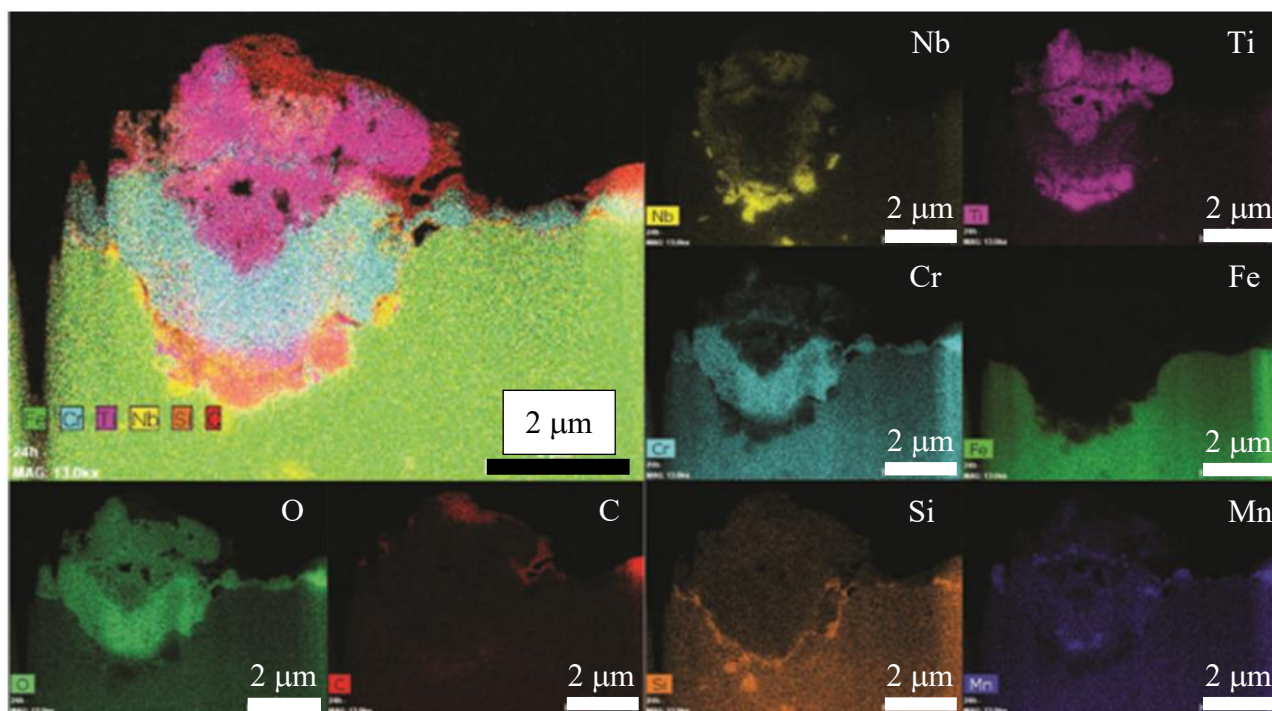


Fig. 4.4. Cross-sectional STEM/EDX maps of the oxide nodule above the grain of AISI 441 after oxidation at 800 °C in O₂-5% H₂O for 24 h. Reproduced from W. Wongpromrat et al., Mater. High Temp. 32 (2015) 22–27 [15].

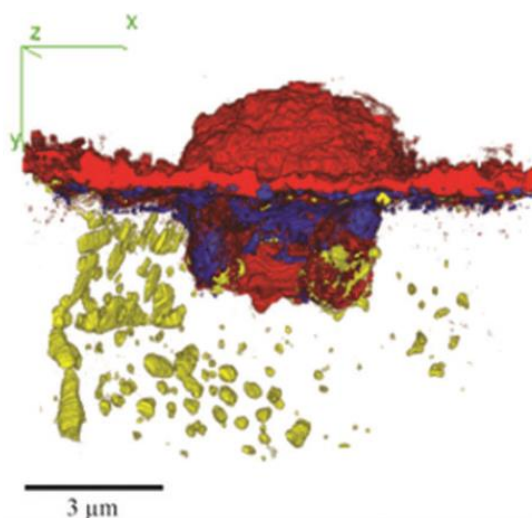


Fig. 4.5. Three dimensional image of the oxide nodule above the grain of AISI 441 after oxidation at 800 °C in O₂-5% H₂O for 24 h (red: oxide layer with chromium and titanium; blue: silicon; yellow: niobium). Reproduced from W. Wongpromrat et al., Mater. High Temp. 32 (2015) 22–27 [15].

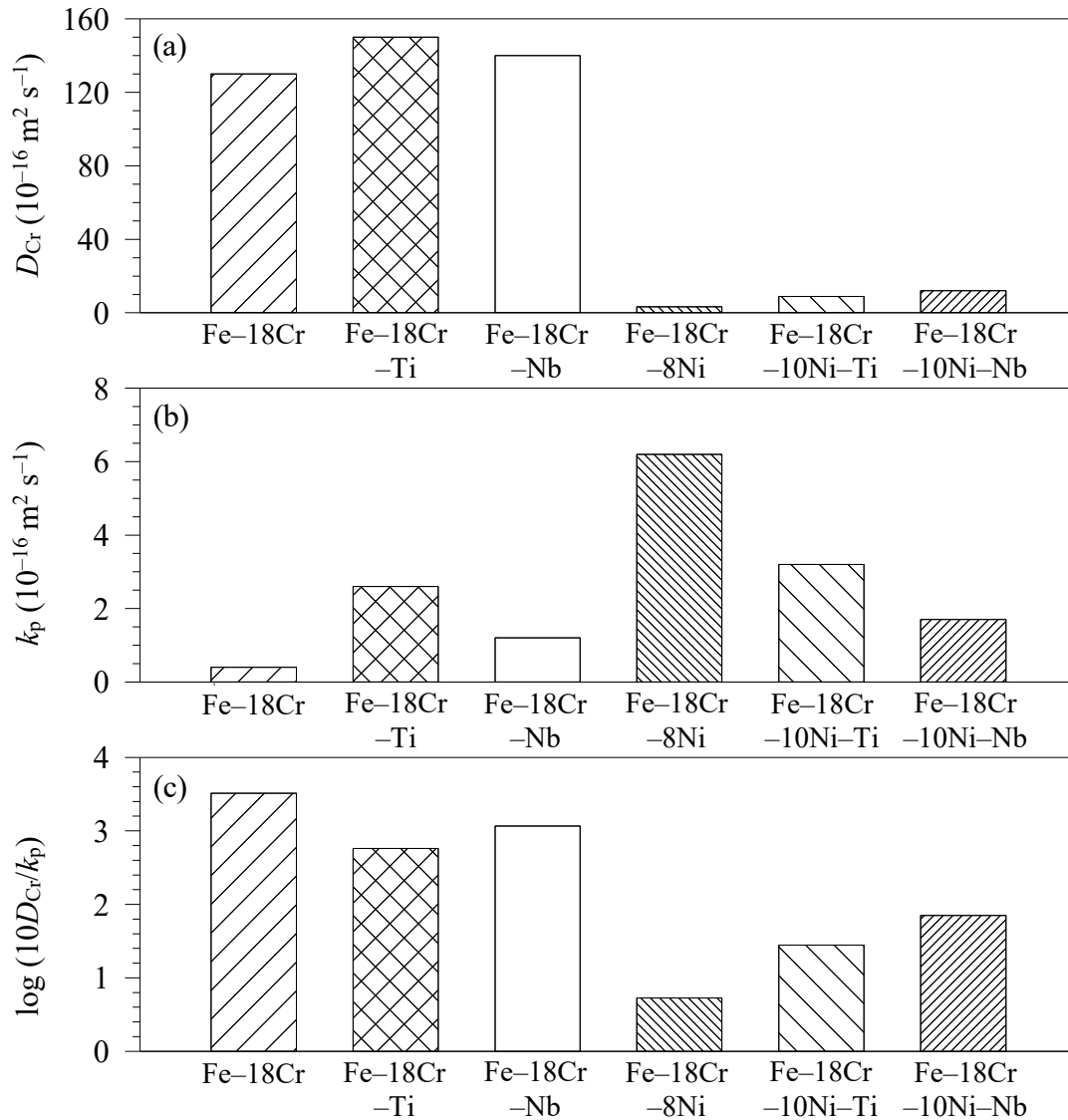


Fig. 4.6. The ratio of diffusivity of chromium in stainless steel to parabolic rate constant of oxidation at 950 °C in laboratory air [17].

Fig. 4.6(a) shows the diffusivity of chromium in stainless steels. It can be seen that the diffusivities of chromium in ferritic steels are faster than those in austenitic ones. This is because the ferritic crystal structure was loosely packed compared with the austenitic one [17]. The addition of stabilisers (titanium and niobium) does not considerably change the chromium diffusivity in ferritic grades as it was observed that the difference in diffusivities between the stabilised grades and the non-stabilised one is only in the range of 8–15%. However, even though the diffusivities of chromium in austenitic grades are relatively low, the addition of stabilisers significantly increases the chromium diffusivity i.e. by about 170 and 264% for the addition of titanium and niobium respectively.

After the isothermal oxidation test at 950 °C in laboratory air up to 60 h, the oxidation kinetics of the studied ferritic stainless steels were parabolic with the accelerated oxidation rate for the stabilised steels as shown in Fig. 4.6(b). Toscan et al. [17] observed that the addition of titanium gave internal oxides which were possibly responsible to the faster oxidation rate. For the austenitic stainless steels, they found that the oxidation rate of Fe-18Cr-10Ni was also parabolic but only up to about 9 h before breakaway oxidation occurred. The addition of stabilisers in austenitic stainless steel could suppress the breakaway oxidation at that early period of oxidation [17]. Fig. 4.6(b) shows the rate constants of the austenitic stainless steels in the parabolic oxidation regime. For the cyclic oxidation test, the oxidation rates of the ferritic stainless steels were still parabolic [17]. On

the contrary, spallation of the thick and porous nodular iron oxides formed on austenitic stainless steels was observed with the greater mass loss for the non-stabilised austenitic stainless steel [17].

As a matter of discussion, the diffusivity of chromium in metal indicates the supply rate of chromium from the metal to the metal/scale interface, while the parabolic rate constant indicates the consumption rate of chromium for oxidation. The ratio of chromium diffusivity to parabolic rate constant could then be used to assess the tendency of chromium depletion at the metal/scale interface which could lead to the formation of the non-protective iron oxides. From the data of chromium diffusivities and parabolic rate constants shown in Figs. 4.6 (a) and (b), that ratio was calculated and plotted in terms of $\log(10D_{\text{Cr}}/k_p)$ as shown in Fig. 4.6(c). It can be seen that the ratios of chromium diffusivity to parabolic rate constant for ferritic grades are about 58–325. These values are considerably higher than those for the austenitic ones which are in the range of 0.5–7.0. One of the major reasons for this difference is that chromium diffusivity in the ferritic grade is faster than that in the austenitic one. The high chromium supply rate could effectively maintain chromium content at the metal/scale interface to form the protective chromia. For the non-stabilised austenitic stainless steels (Fe–18Cr–10Ni), this ratio is about 0.53. The very low ratio indicates that the chromium supply rate is not enough to maintain the chromium content at the metal/scale interface to form the protective chromia and thus the breakaway oxidation is possible. The addition of stabilisers could increase chromium diffusivity in the austenitic matrix as shown in Fig. 4.6(a), contributing to the increased ratio of chromium diffusivity to parabolic rate constant as shown in Fig. 4.5(c). As a result, the suppression of the breakaway oxidation is possible. The addition of stabilisers is then required for austenitic grades for this purpose.

Titanium and niobium do not only affect the chromium diffusion in the steel and the oxidation rate constant, they also affect the scale adhesion. Mougin et al. [18] investigated the effects of stabilisers on the adhesion of scale on stainless steels. In this work, Fe–18Cr, Fe–18Cr–0.14Ti–0.47Nb, Fe–18Cr–0.45Ti and Fe–18Cr–0.44Nb were oxidised at 900 °C in Ar–15% O₂. For the grades containing titanium, the nodular titania was observed on top of the oxide scale as well as along the metal grain boundary including the one at the metal/scale interface. For the grades containing niobium, the Fe₂Nb intermetallic was also found along the metal grain boundary. It was also observed that the spontaneous spallation of the oxide scale on Fe–18Cr–Ti was drastically reduced compared to the oxidised Fe–18Cr and Fe–18Cr–Nb respectively. Those samples were further subjected to the inverted blister test for the scale adhesion assessment. It was found that the adhesion energy of the scale on Fe–18Cr–Ti was drastically higher than that of the scale on Fe–18Cr–Nb, while the adhesion energy of the scale on Fe–18Cr–Ti–Nb was between those former two values and slightly lower than the adhesion energy of the scale on Fe–18Cr. In case of Fe–18Cr–Ti, after the inverted blister test the scale and stainless steel substrate were debonded as schematised in Fig. 4.7. It is seen that the TiO₂ which precipitates at the metal/scale interface remains in the metal side while the oxide scale including Cr–Mn spinel, chromia and silica (when existing) are removed from the substrate. This result exhibits the mechanical keying effect of TiO₂ on improving the scale adhesion. On the contrary, in case of Fe–18Cr–Ti–Nb, even though TiO₂ nodule exists at the metal/scale interface, the formation of Fe₂Nb is found to be under the titania nodule. This Fe₂Nb reduces the adhesion of the nodular titania to the metal substrate, and as a result after the inverted blister test the oxide scale together with the nodular titania is detached from the metal substrate. For the other stainless steels, the Fe–Mo intermetallic compound was also observed at the interface between scale and the AISI 444 stainless steels. Its effect on reducing the scale adhesion was also reported [19].

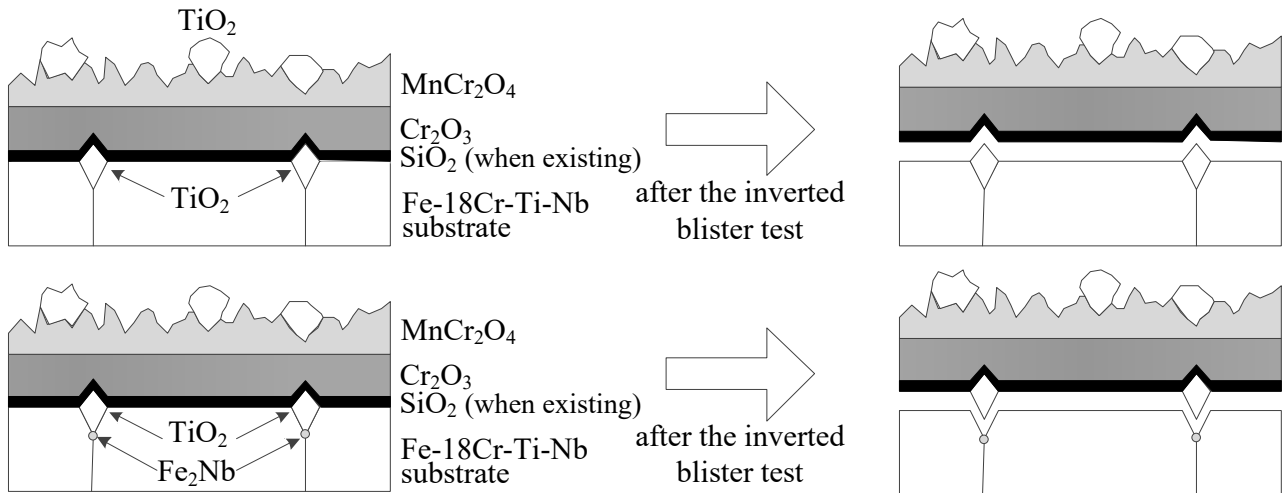


Fig. 4.7. Schematic sketch showing the roles of titanium and niobium on the adhesion of scale to Fe-18Cr-Ti-Nb stainless steel. Redrawn and adapted from J. Mougin et al., *Mater. Sci. Eng. A* 359 (2003) 44–51 [18].

4.2.3 Effects of Reactive Elements

Reactive element (RE) is the element that is more active to oxygen than the elements that form the oxide scale i.e. chromium and aluminium [20, 21]. These elements are such as yttrium, lanthanum, zirconium, cerium and hafnium [21, 22]. The addition of the reactive elements could change the growth mechanism of the oxide, thus affecting behaviour and properties of the oxide-steel system e.g. the selective oxidation, the oxidation rate and the scale adhesion.

For the chromia-forming stainless steel, the thermal scale is typically chromia topped by the spinel of manganese and chromium [19]. Comparing to the undoped steel, when the reactive element is alloyed it was reported that this element could reduce the alloy grain size and therefore increase the cationic outward flux, thus promoting the formation of the protective chromia scale earlier [21]. Furthermore, when the oxidation proceeds, it was reported that the reactive element tends to diffuse to the scale/gas interface via the oxide grain boundary where it segregates. Because the ionic radius of the reactive element is typically bigger than that of chromium, the reactive element segregation thus blocks the outward chromium diffusion resulting in the reduced oxidation rate [21, 23].

The other beneficial effect of the reactive element is to improve the scale adhesion. The example of this effect exhibits in Fig. 6.4 in Chapter 6 that shows the oxide scale on Crofer 22 APU (Fe-22Cr-La-Ti) and AISI 441 stainless steels oxidised in air and water vapour before and after the tensile test for scale adhesion assessment. It can be seen that the scale on Crofer 22 APU which contains lanthanum well adheres to the substrate while the scale on AISI 441 is spalled under the imposed strain [24]. The mechanism proposed to explain the improved scale adhesion by the reactive element is the surface sulphur cleaning effect suggesting that the interaction between the reactive element and sulphur could reduce the sulphur segregation at the metal/scale interface [23, 25]. The other mechanism proposed is the reduction of void formation by the reactive element. This might be because the reduction of the cationic outward diffusion resulted in the lower vacancy injection to the metal/scale interface [23, 26]. It was also proposed that the reactive element might reduce the surface energy, thus reducing the driving force for void formation and therefore the formation of interfacial voids [22, 23].

4.3 Alumina-Forming Stainless Steels

4.3.1 High Temperature Oxidation of Alumina-Forming Stainless Steels

Most of commercial stainless steels form a protective Cr_2O_3 scale when exposed at higher temperatures in oxidising atmospheres. The Cr_2O_3 scale shows good oxidation resistance but it is much less protective compared to an Al_2O_3 scale. Al_2O_3 is one of the most thermodynamically stable oxides and protects the alloy substrate even at the temperatures higher than 1300 °C. Heat resistant steels which are protected by an Al_2O_3 scale are, therefore, expected to have excellent oxidation resistance and extended lifetime at higher temperatures. However, because there are several problems for Al_2O_3 -forming alloys, commercial grade of Al_2O_3 -forming stainless steels has not been widely used.

One of the typical problems of the Al_2O_3 -forming alloys is formation of Al_2O_3 scale at the temperatures of most of heat resistant alloys are used. The temperatures in which most of heat resistant steels are used as the components of chemical plants, incinerators, boilers, etc. are not so high, ~800 °C. At such temperature region, Al_2O_3 scale formation is difficult. Fig. 4.8 shows the example of initial Al_2O_3 formation on a Fe–24Cr–10Al (at.%) stainless steel measured by *in-situ* high-temperature XRD using a synchrotron source [27]. In this test, the specimen was exposed to air and heated with the heating rate of 50 °C min⁻¹ to 1000 °C. Then the sample was held isothermally at 1000 °C for 1 h in the same atmosphere. During the experiment, i.e. heating, isothermal oxidation and cooling, the XRD measurement was conducted on the sample surface every 10 s using 6 s for data collection in each measurement. Initial Al_2O_3 formation is always observed at the temperatures above 800 °C.

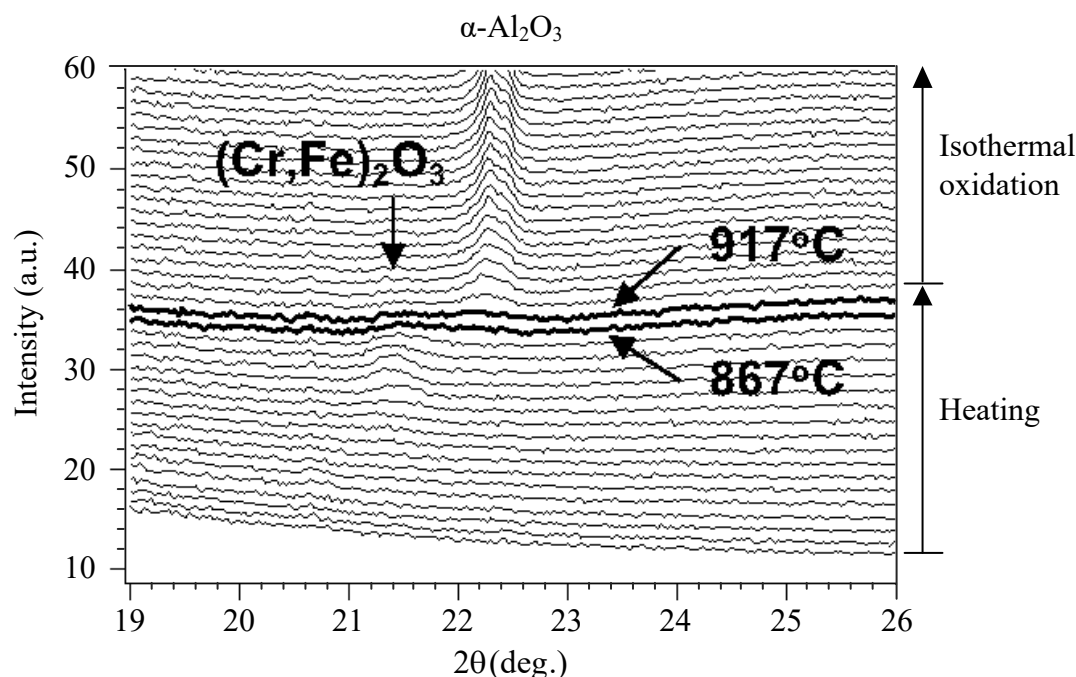


Fig. 4.8. *In-situ* high-temperature XRD patterns of oxide scale formed on Fe–24Cr–10Al (at.%) heating to 1000 °C. Redrawn and adapted from S. Yoneda et al., *Oxid. Met.* 89 (2018) 81–97 [27].

The second problem is the preferential formation of a less protective metastable Al_2O_3 . Although this problem will be discussed below, metastable Al_2O_3 scale formation is not avoided on the alloys with high aluminium contents and nickel-based alloys even though the alloys are oxidised at temperatures over 1100 °C.

In addition, high alloy aluminium contents are also not acceptable for heat resistant steels. As a matter of fact, despite the requirement of a sufficient aluminium content in the alloy for the formation of a protective Al_2O_3 scale, aluminium additions are usually very limited because of the adverse effect of aluminium on the ductility, weldability, and fabricability of the substrate. Thus, aluminium concentration in the substrate needs to be lowered as much as possible.

Currently, most of successful commercial Al_2O_3 -forming stainless steels are ferritic stainless steels. They are used in metal honeycombs of automobile emission system i.e., catalytic converters and in heating wires, which are usually used at temperatures more than 1100 °C. In the Sections 4.3–4.5, the oxidation behaviour of Al_2O_3 -forming stainless steels, which contain not only steels called as “stainless” but also iron-based alloys which form a protective Al_2O_3 scale, will be discussed.

4.3.2 Metastable and Stable Alumina Scale Formation

It is well-known that Al_2O_3 has several isomorphous structures, such as γ , θ , and α - Al_2O_3 . Among those Al_2O_3 phases, γ , θ - Al_2O_3 are metastable phases and transition eventually to α - Al_2O_3 [28, 29]. When Al_2O_3 -forming alloys are oxidised, a metastable Al_2O_3 scale is usually formed initially, and it later transforms to the stable Al_2O_3 scale [30–33]. This initial metastable Al_2O_3 formation is one of the issues for the use of Al_2O_3 -forming alloys, because the transition to α - Al_2O_3 takes longer time at lower temperatures [31] and the growth rate of metastable Al_2O_3 is much higher than that of stable Al_2O_3 scale [34, 35]. In order to accelerate the transformation, much attention has been paid towards understanding the mechanism of the metastable-stable Al_2O_3 transformation [36–39], even though the details of the mechanism, particularly for the thermally grown oxide scale of Al_2O_3 , have not been fully understood yet.

Tanigushi and Andoh [31] studied the isothermal transformation of Al_2O_3 scales formed on Fe–Cr–Al alloys with/without aluminium-deposition. In the air oxidation between 1073–1373 °C, they found that transformation to α - Al_2O_3 occurs in shorter time at higher temperatures on both samples. Regarding aluminium contents, it is clear that transformation is delayed on the alloys with higher surface aluminium contents. Higher aluminium addition in alloys is also detrimental for rapid formation of α - Al_2O_3 .

This delayed transformation on the alloy is strongly related to the initial transient oxidation behaviour of alloys. Transformation of metastable to stable α - Al_2O_3 scale is known to be accelerated by the presence of Fe_2O_3 and/or Cr_2O_3 scale. The beneficial effect of such oxides is referred as the “template” effect, since Fe_2O_3 and Cr_2O_3 have the same corundum crystal structure as α - Al_2O_3 . Those oxides act as a “template” for the nucleation of α - Al_2O_3 . From the previous studies, the template effect is interpreted as a precipitation of α - Al_2O_3 from the transient Fe_2O_3 with Al_2O_3 saturation [35, 40–43]. Hayashi et al. [44] studied the meta-stable phase transformation behaviour of Al_2O_3 scale on Fe–Ni–Al alloys. They found that the oxidation mass gain tended to be reduced with the increased iron content in the alloy. The increased iron content in the alloy reduced the time needed for the transition from the rapid oxidation stage in the early period to the slower oxidation stage in the later stage. Fig. 4.9 shows the phase transformation behaviour of Al_2O_3 scale which formed on Fe–41.5Al (at.%), Ni–41Al–41Fe (at.%) and Ni–41.5Al (at.%) [44]. It was found that high iron content is beneficial and promotes the rapid transformation to α - Al_2O_3 . The samples on which α - Al_2O_3 developed rapidly always formed Fe_2O_3 prior the formation of Al_2O_3 scale in the transient oxidation period as indicated in Fig. 4.9(d). However, transformation to α - Al_2O_3 is delayed when alloys are oxidised in atmospheres where the oxygen partial pressure is lower than that of formation of Fe_2O_3 [45]. Iron-based stainless steels might have advantage to form α - Al_2O_3 due to initial Fe_2O_3 or Cr_2O_3 formation. However, rapid establishment of α - Al_2O_3 results in smaller α - Al_2O_3 grain sizes [46], which might influence its growth rate of the α - Al_2O_3 scale.

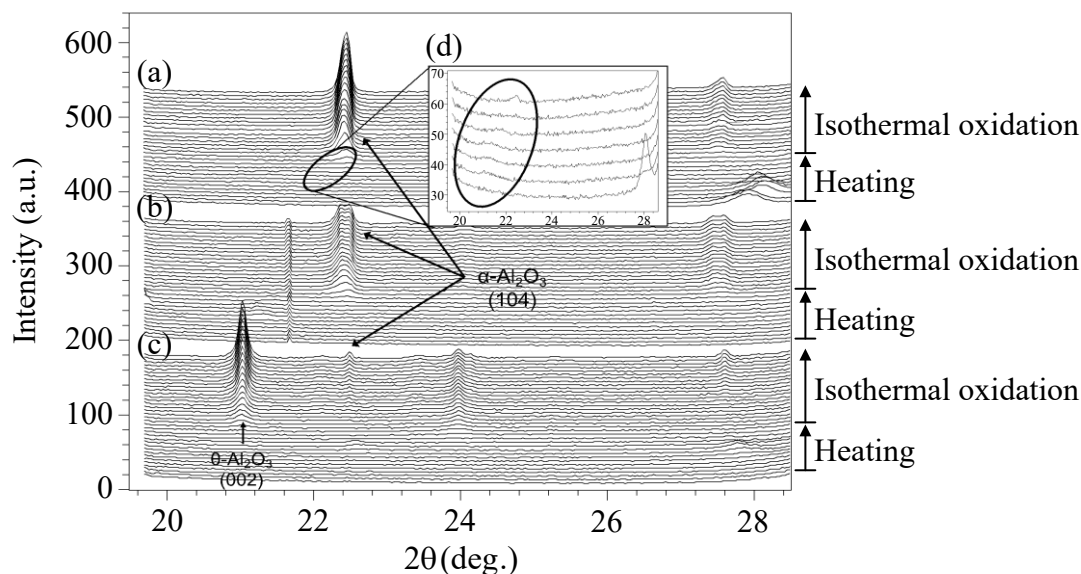


Fig. 4.9. *In-situ* high-temperature XRD patterns of oxide scale formed on (a) Fe–41.5Al (at.%), (b) Ni–41Al–41Fe (at.%), (c) Ni–41.5Al (at.%) and (d) Fe–41.5Al (at.%) which is the enlarged patterns of (a) during heating with the rate of $20\text{ }^{\circ}\text{C min}^{-1}$ to $1000\text{ }^{\circ}\text{C}$ followed by isothermal oxidation up to 1 h. Redrawn and adapted from S. Hayashi et al., *Oxid. Met.* 86 (2016) 151–164 [44].

4.4 Alumina-Forming Ferritic Stainless Steel

4.4.1 Effect of Chromium

As mentioned above, higher aluminium additions to the alloy substrate are restricted. Chromium additions are known to reduce the critical aluminium content to form a protective Al_2O_3 scale. Therefore, most of the commercial Al_2O_3 -forming stainless steels contain relatively high chromium contents, in the range 13–20%. The composition of Al_2O_3 -forming steels is typically Fe–20Cr–10Al (at.%) with additions of small amounts of various reactive elements such as yttrium, cerium, lanthanum, zirconium and so on. Regarding the mechanical properties of alloy, higher chromium content is detrimental due to the possibility of formation of the brittle chromium-rich bcc phase (α') in the ferritic (α) matrix of Fe–Cr–Al system because the miscibility gap at lower temperatures. For the Fe–Cr–Al system in the region of ferrite substrate with an aluminium content about 10 at.% at $475\text{ }^{\circ}\text{C}$ [47], the maximum chromium content allowed in order to avoid α' precipitation is about 12–15 at.%. The Al_2O_3 -forming stainless steels are usually used at higher temperatures more than $1000\text{ }^{\circ}\text{C}$. Therefore, α' formation can be neglected during service time. However, if high-chromium stainless steels are exposed at lower temperatures for longer times, embrittlement due to precipitation of α' -phase should be considered.

The effect of chromium on promoting Al_2O_3 scale formation on the substrate with low aluminium contents has been widely investigated. It is believed that the initially formed Cr_2O_3 scale decreases the oxygen potential at the metal/scale interface, which decreases inward oxygen diffusion in the substrate, thus promoting a protective Al_2O_3 scale without internal aluminium oxidation [48–50]. Wagner suggested this effect of chromium as an “oxygen getter” [51]. Yoneda et al. [27, 52] investigated the initial oxidation behaviour of Fe–Cr–Al alloys with 4–24 at.% of chromium to verify this mechanism by the *in-situ* high-temperature XRD technique using a synchrotron source. Fig. 4.10 shows XRD patterns of Fe–6Al (at.%) and Fe–4Cr–6Al (at.%) alloys during heating to $1000\text{ }^{\circ}\text{C}$ in air and the cross-section of the oxide scale after isothermal oxidation at $1000\text{ }^{\circ}\text{C}$ for 1 h [52]. The diffracted signals obtained from both alloys during heating are only Fe_2O_3 . However, an exclusive Al_2O_3 scale has developed on Fe–4Cr–6Al (at.%) after 1 h of oxidation. They also found that the addition of chromium by 24 at.% to Fe–6Al (at.%) alloy does not prevent internal oxidation at the initial oxidation during heating. Apparently, an initial Cr_2O_3 scale formation cannot be the

main reason for promoting Al_2O_3 scale formation. The interdiffusion coefficients of aluminium in the Fe–Cr–Al system at 1000 °C was evaluated [53] and the results suggested that chromium-depletion in the subsurface region in the initial oxidation period may enhance the aluminium outward diffusion flux due to the positive cross-term coefficient, which promotes the Al_2O_3 scale formation. Airiskallio et al. [54] also made the discussion similar to this “cross-term” effect. Additionally, it is remarked that the alumina morphology is the opposite of the chromia one, and composed of an inner columnar and an outer equiaxed subscales.

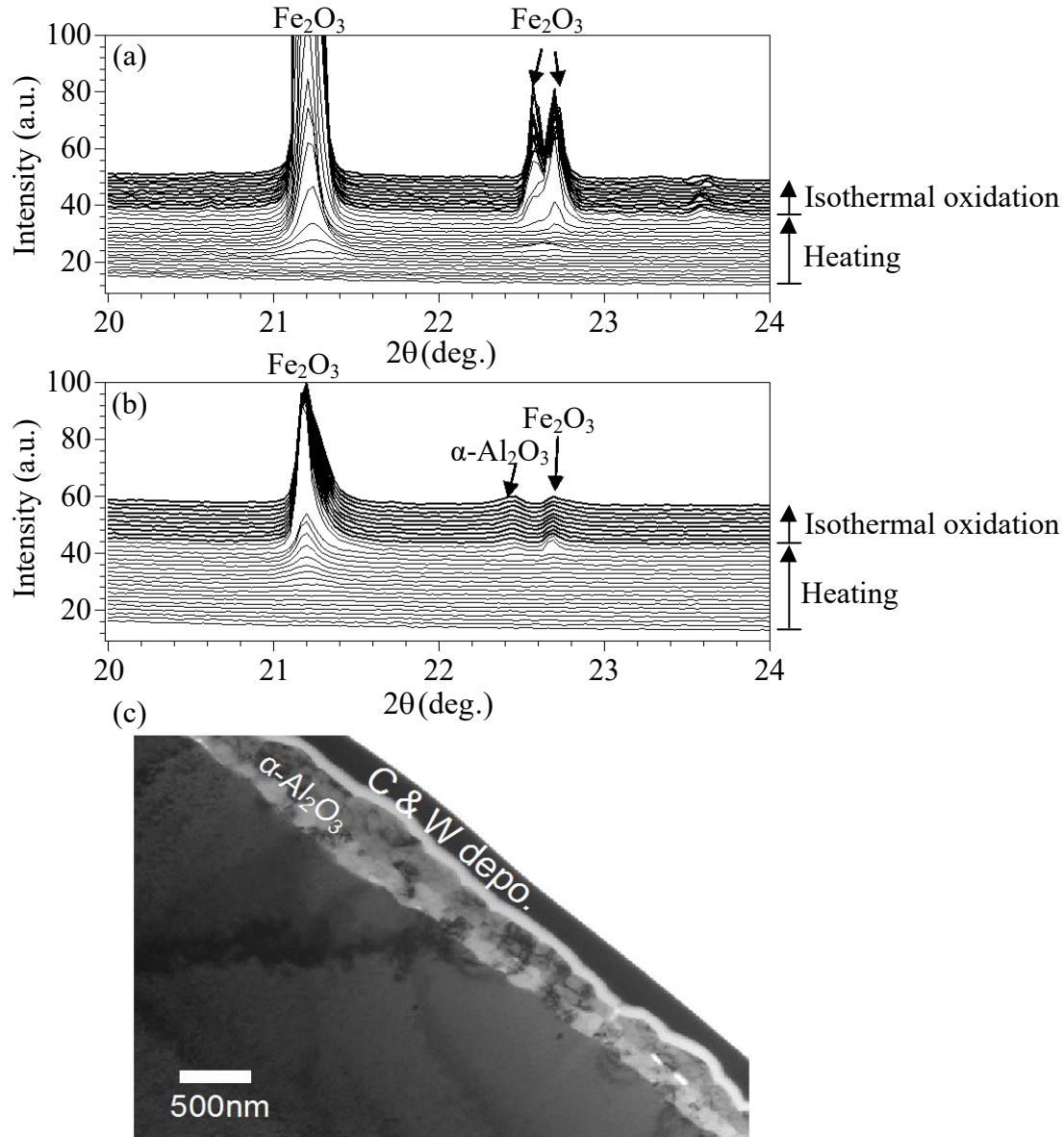


Fig. 4.10. *In-situ* high-temperature XRD patterns of (a) Fe–6Al (at.%) and (b) Fe–4Cr–6Al (at.%) alloys during heating, and (c) the TEM cross-section of Fe–4Cr–6Al (at.%) alloy after oxidation at 1000 °C in air for 1 h. Redrawn and adapted from S. Yoneda et al., *Oxid. Met.* 86 (2016) 357–370 [52].

4.4.2 Effect of Refractory Elements

In order to satisfy the demand to reduce the greenhouse gas and fuel consumption rate, the operation temperature of recent automobile engines is increasing to improve the thermal efficiency. Therefore, even though the Al_2O_3 -forming ferritic stainless steels are predominantly used for catalytic converters, increasing the strength at higher temperature of the steels is still required. In order to increase the strength of the steels, refractory metals such as molybdenum, tungsten and tantalum are used as solid-solution hardening elements. Among those elements, molybdenum is

widely used for Fe–Cr–Al steels which are used for not only the catalytic system but also heating elements. The addition of molybdenum is reported to reduce the oxidation performance of Fe–Cr–Al–La and Fe–Cr–Al–La–Zr alloys by increasing the growth rate of the Al_2O_3 scale [55, 56]. Mizutani et al. [56] investigated the detrimental effect of molybdenum on the oxidation of Fe–Cr–Al–La–Zr alloys and found that molybdenum reduces the beneficial effect of lanthanum and zirconium on Al_2O_3 scale growth as shown in Fig. 4.11.

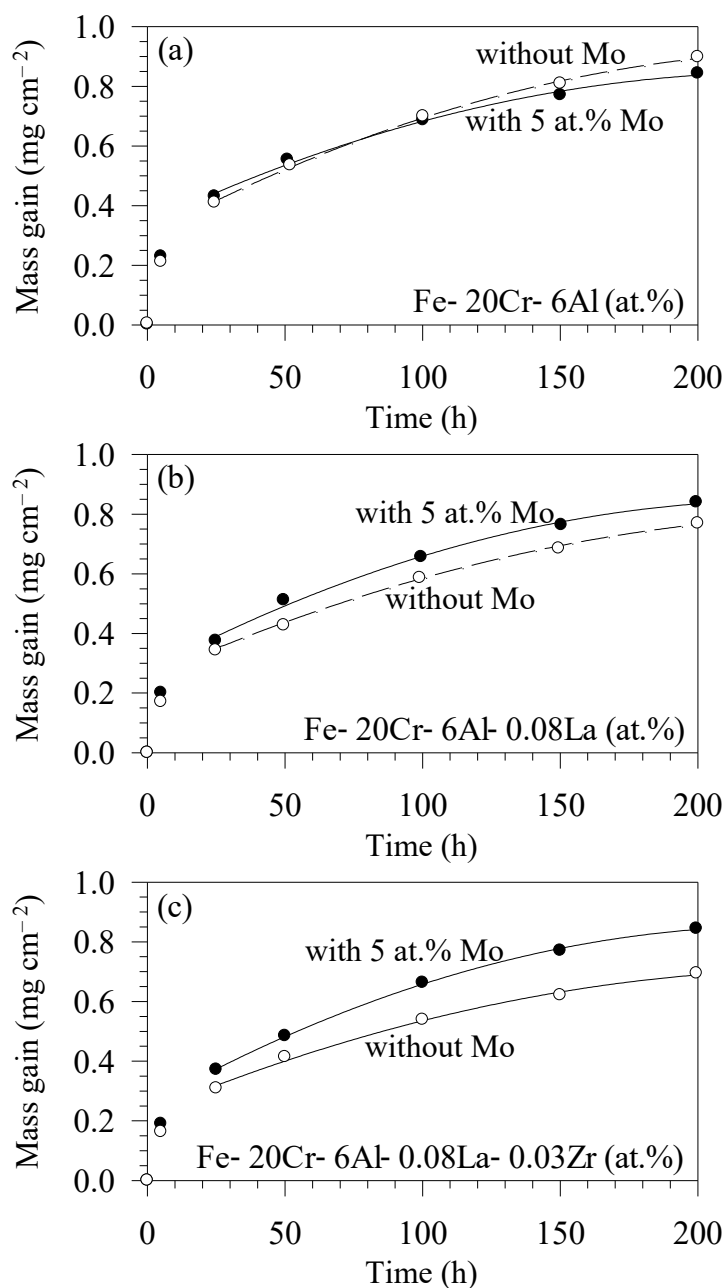


Fig. 4.11. Effect of molybdenum addition on the oxidation kinetics of (a) Fe–20Cr–6Al (at.%), (b) Fe–20Cr–6Al–0.08La (at.%) and (c) Fe–20Cr–6Al–0.08La–0.03Zr (at.%) during oxidation at 1100 °C in air. Redrawn and adapted from A. Mizutani et al., *Oxid. Met.* 87 (2017) 109–124 [56].

As it will be shown in following section, reactive elements greatly reduce the growth rate of Al_2O_3 scales by reducing grain boundary diffusivities of anion and oxide ions via their grain boundary segregation. The results by Mizutani et al. [56] indicated that molybdenum additions reduce the grain boundary segregation of reactive elements and eliminate the blocking effect of reactive elements for ion diffusion. They concluded that higher reactive element additions are

necessary for molybdenum-containing alloys in order to reduce the growth rate of Al_2O_3 scales to similar levels as the Al_2O_3 scale formed on the alloys without molybdenum. This detrimental effect of molybdenum was speculated to be caused by molybdenum reducing the thermodynamic activity of lanthanum and/or zirconium in the Fe–Cr–Al substrate.

4.4.3 Effect of Reactive Elements

Similar to the case of chromia-forming stainless steels, reactive elements have two important effects on the oxidation of alumina-forming steels. They increase the adhesion and reduce the growth rate of an Al_2O_3 scale [57]. Various mechanisms to increase adhesion of the scale have been proposed such as sulphur and/or carbon gettering, keying effect and void formation suppression at the metal/scale interface [57–59]. The reduced Al_2O_3 scale growth rate by the reactive element additions is explained by their segregation at grain boundaries [22]. The grain boundary diffusivity of anion and oxide ions in Al_2O_3 is greatly reduced by doping with reactive elements [60]. Among those beneficial effects, Pint et al. [61] suggested that improved adhesion of the Al_2O_3 scale is the most important effect for increasing the lifetime of steels. However, reduction of the growth rate by reactive element additions is also an important effect, particularly for foils and heating elements, since aluminium supply from the matrix in thin foils and wires is very limited.

Over-doping of reactive elements in alloys causes rapid oxidation, thus optimisation of reactive element concentrations is strongly required [61, 62]. Because the tolerance of concentration of reactive elements depends on reactive elements and alloy systems, it is necessary to establish the method to find the best concentration of reactive elements. Shizukawa et al. [63] investigated the oxidation behaviour of ODS Fe–Cr–Al– Y_2O_3 alloys with different excess oxygen, which is the total content of oxygen subtracted by the one used to form Y_2O_3 during the alloy production, to control the activity of yttrium, a_Y , in the substrate. Fig. 4.12 shows the effect of excess oxygen on the oxidation mass gain of an ODS alloy of composition Fe–7Al–15Cr–0.5Ti–0.4Zr–0.5 Y_2O_3 at 1200 °C in air. Lower excess oxygen level causes higher oxygen mass gain due to over-doping of zirconium, but oxidation mass gain drastically decreases on the alloys with higher excess oxygen content. Based on the result shown in Fig. 4.12, they suggested that over-doping by zirconium is strongly related to the stability of ZrO_2 and Al_2O_3 in the alloy substrate, i.e. activity of zirconium (a_{Zr}) and Al (a_{Al}) which are given by Eq. 4.31.

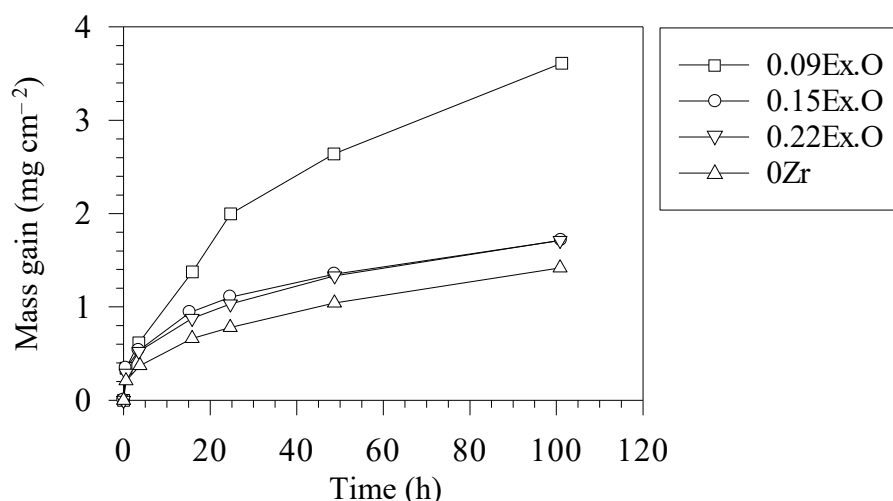


Fig. 4.12. Oxidation kinetics of Fe–7Al–15Cr–0.5Ti–0.4Zr–0.5 Y_2O_3 with excess oxygen at 1200 °C in air. Redrawn from Y. Shizukawa et al., The effect of excess oxygen on the high temperature oxidation in zirconium added FeCrAl ODS steels, in: Y. Murata et al. (Eds.), Proceedings of the First International Conference on Advanced High-Temperature Materials Technology for Sustainable and Reliable Power Engineering, Japan, 2015, pp. 149–152 [63].

$$a_{\text{Zr}} < a_{\text{Al}}^{4/3} \left[\frac{\exp\left(\frac{\Delta G_{\text{ZrO}_2}^\circ}{RT}\right)}{\exp\left(\frac{\Delta G_{\text{Al}_2\text{O}_3}^\circ}{RT}\right)} \right] \quad (4.31)$$

where R is the gas constant, T is the absolute temperature, $\Delta G_{\text{ZrO}_2}^\circ$ and $\Delta G_{\text{Al}_2\text{O}_3}^\circ$ are the Gibbs free energies of formation of ZrO_2 and Al_2O_3 , respectively. Gheno et al. [64] also proposed a similar mechanism for hafnium-tolerance in $\gamma + \gamma'$ Ni–Cr–Al alloys. They further suggested that the level of hafnium content varies due to structural changing of alloy subsurface region by the selective oxidation of aluminium because γ' dissolution in the substrate [64]. Thus, the factors which may control the activities of aluminium and reactive elements are expected to affect the optimised concentration of reactive elements. Optimisation of reactive element concentration is one of the most important factors for producing higher oxidation resistant commercial stainless steels. Therefore, further studies are still necessary.

Because the Al_2O_3 scale grows mainly by grain boundary diffusion at the temperature range of our interest, the microstructure of the Al_2O_3 and its evolution during oxidation strongly affect the growth rate of the Al_2O_3 scale. Naumenko et al. [65] reported that the grain size of columnar grains of an inwardly growing Al_2O_3 scale formed on Fe–Cr–Al–Y alloy at 1200 °C in air linearly increases with the depth from the gas/scale interface. They supposed that coarsening of columnar grains, i.e. lateral growth of the grains, does not occur during oxidation. However, our recent study clearly indicated that the columnar grains of Al_2O_3 formed on Fe–Cr–Al alloys without reactive elements showed grain coarsening with oxidation time [66].

Fig. 4.13 shows the size of columnar grains of the Al_2O_3 scale formed on Fe–Cr–Al alloy without and with different zirconium contents as a function of the distance from the outer/inner interface at 1000 °C. Figs. 4.13 (a), (b) and (c) show the results for the Fe–20Cr–10Al (at.%), Fe–20Cr–10Al–0.01Zr (at.%) and Fe–20Cr–10Al–0.1Zr (at.%) respectively as a function of distance from the outer/inner interface at 1000 °C in air [66]. The solid and blank circles in the figures indicate the samples after oxidation for 100 and 400 h, respectively. It can be seen that grain coarsening is not observed for up to 400 h on the alloy with 0.1 at.% of zirconium and for up to 100 h on the alloy with 0.01 at.% of zirconium. However, grain coarsening is observed on the alloy without zirconium after 100 h and alloy with 0.01 at.% of zirconium after 400 h. Apparently zirconium prohibits the grain coarsening of Al_2O_3 during oxidation, resulting in smaller columnar grain sizes. A similar effect of zirconium on the formation of a fine grained Al_2O_3 scale formed on Fe–Cr–Al–Y–Zr alloy at 1200 °C in air was also observed [67]. Zirconium obviously has an effect on the microstructure of Al_2O_3 scale. Moreover, not only the growth rate of the scale, but also different properties such as its adhesion and creep deformation should be controlled by the microstructure of Al_2O_3 scale. Thus, it would be interesting to investigate the effect of different reactive elements on the microstructure of the Al_2O_3 scale.

4.5 Alumina-Forming Austenitic Stainless Steels

As mentioned previously, Al_2O_3 scale formation is difficult at relatively lower temperatures. Therefore Al_2O_3 -forming stainless steels are expected to be used at much higher temperatures compared to Cr_2O_3 -forming steels. The temperature capability of most of the stainless steels with ferritic substrate is much lower than that of austenitic steels, and as a result ferritic FeCrAl alloys are not used at higher temperatures even they have excellent oxidation resistance. Structural components such as boiler tubes and turbine blades need to have sufficient high-temperature strength. These components should employ the austenitic matrix, which has much higher

mechanical strength. However, commercial “Al₂O₃-forming austenitic stainless steels” have not been well developed.

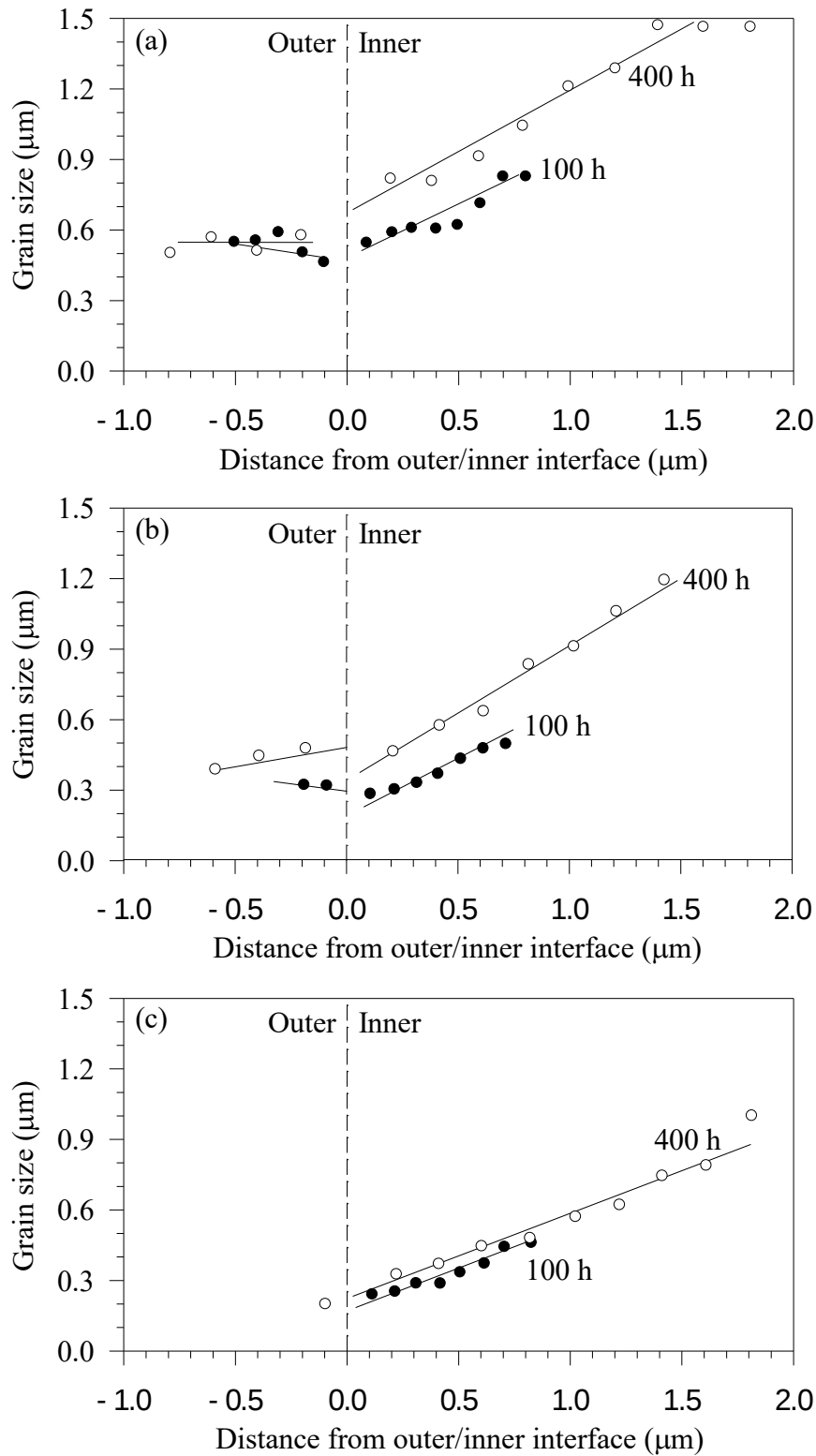


Fig. 4.13. Grain size of outer equiaxed and inner columnar Al₂O₃ grains formed on (a) Fe-20Cr-10Al (at.%), (b) Fe-20Cr-10Al-0.01Zr (at.%) and (c) Fe-20Cr-10Al-0.1Zr (at.%) as a function of distance from the surface at 1000 °C in air after oxidation for 100 h (solid circles) and 400 h (blank circles) [66].

Compared to ferritic stainless steels, austenitic steels need higher aluminium contents to form an exclusive Al_2O_3 scale because the much lower diffusivity of aluminium in the fcc structure than that in the bcc is expected [68, 69]. Similar to the case of ferritic steels, maximum aluminium additions to the austenitic substrate are also very limited. Aluminium is very strong bcc stabiliser in this system, therefore, addition of aluminium in the austenitic Fe–Ni–Cr substrate results in A2-bcc and/or B2-bcc phase formation. From the Fe–25Ni–15Cr–Al (at.%) phase diagram calculated by FactSage software [70], although the accuracy of this diagram is low particularly at lower temperature region, it is clear that aluminium addition promotes formation of A2 and B2 phases. A2 phase formation decreases high-temperature mechanical properties. Precipitation of B2 phase in the fcc substrate could increase the mechanical strength. However, it also decreases the oxidation performance because aluminium concentration in the substrate is decreased due to aluminium consumption by the B2 phase formation. Fig. 4.14 shows the oxidation behaviour of Ni–20Cr–10Al (at.%) with different iron contents [71]. All alloys have an austenite matrix with B2 precipitates at 1000 °C. Oxidation mass gain increases with increasing iron content in the alloy. The aluminium content in the substrate was found to decrease with the increase of iron content in the alloy i.e. from 8 at.% for 20Fe–50Ni–20Cr–10Al (at.%) to 6 at.% for 40Fe–30Ni–20Cr–10Al (at.%). This decrease was due to the increase in the volume fraction of B2 phase from 0.08 to 0.15%, which results in formation of a protective Al_2O_3 scale difficult. B2-(Ni,Fe)Al phase formation is clearly detrimental for an exclusive Al_2O_3 scale formation.

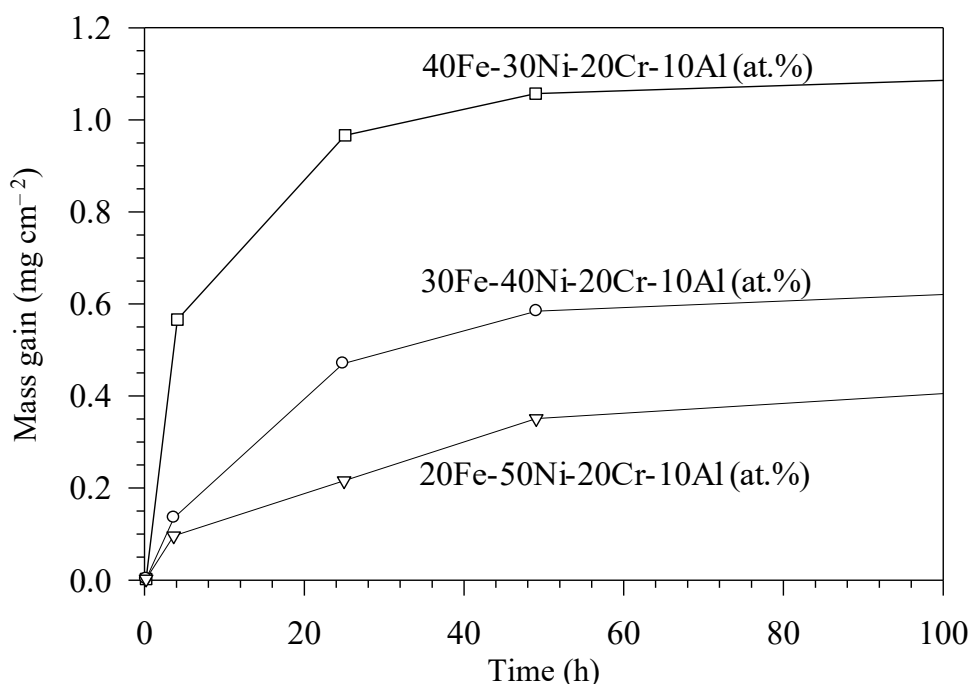


Fig. 4.14. Oxidation kinetics of Fe–Ni–20Cr–10Al (at.%) with different Fe/Ni ratios at 1000 °C in air [71].

Brady et al. [72–74] in Oak Ridge National Laboratory proposed Al_2O_3 -forming wrought and cast austenitic steels. Their proposed steels contain 20–30 wt.% of nickel, 12–20 wt.% of chromium, 0.6–3.0 wt.% of niobium, 0.1 wt.% of carbon and 2.5–5.0 wt.% of aluminium and are strengthened by MC carbide and Fe_2Nb laves phases. These alloys show good high-temperature creep strength but aluminium level is very critical for an exclusive Al_2O_3 scale formation, suggesting that a higher aluminium level is necessary. Although they supposed that B2-NiAl may act as a reservoir compensating the aluminium consumption by Al_2O_3 scale formation, higher aluminium addition promoted the B2-NiAl formation. This result is different from our previous study as shown in Fig. 4.14.

We are now investigating new Al_2O_3 -forming austenitic stainless steels [75]. The target of this steel development is to alternate current conventional Cr_2O_3 -forming austenitic stainless steels such as grade 310, 308 steels, which are produced by conventional techniques such as hot-rolling. The strategy for our alloy design is to produce steels with B2-free austenite matrix, allowing production by conventional processing. Fig. 4.15 shows the effect of copper content on oxidation mass gain of copper-modified Fe–17Ni–17Cr–7Al–0.06Zr (at.%) alloy at 1000 °C in air [75]. Small addition of copper, ~4 at.%, promotes a protective Al_2O_3 scale formation and was found to decrease the critical aluminium content for an Al_2O_3 scale formation, although the detailed mechanism of this beneficial effect of copper is not known yet. The oxidation resistance of these new austenitic steels can be increased by an exclusive Al_2O_3 scale formation.

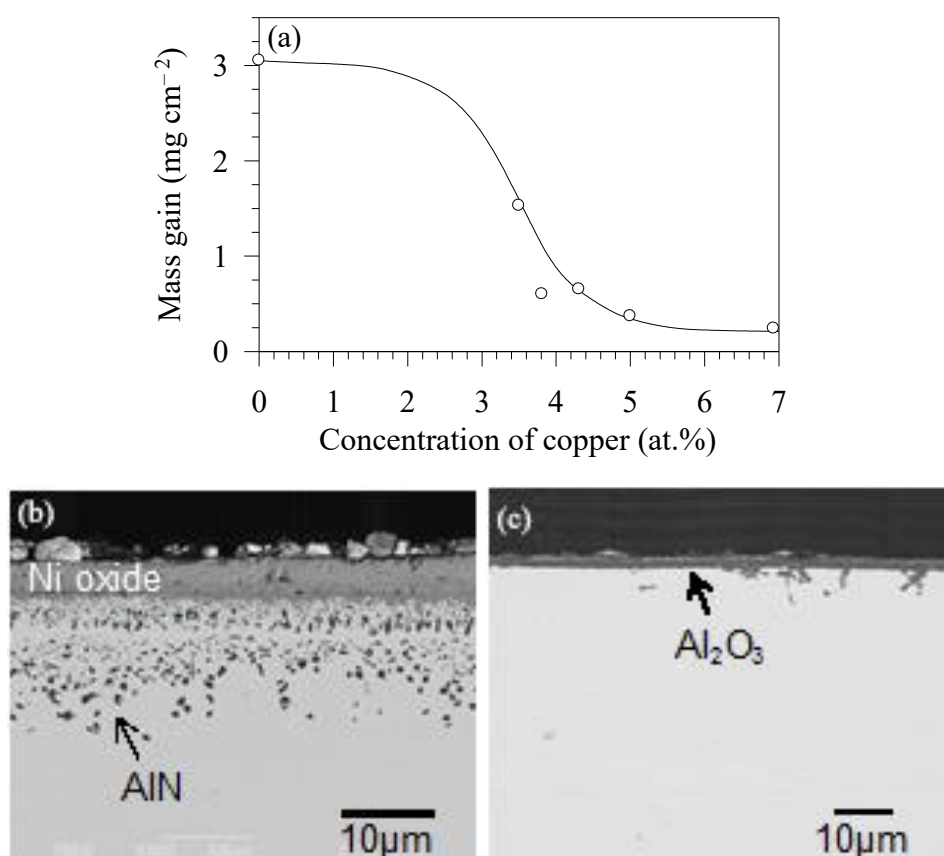


Fig. 4.15. Effect of copper on the oxidation mass gain of Fe–17Ni–17Cr–8Al–xCu–0.06Zr (at.%) alloys after 100 h of oxidation at 1000 °C in air. (a) Oxidation mass gain as a function of copper content, and cross-sections of (b) 0 at.% copper and (c) 5 at.% copper alloys after oxidation. Reproduced and adapted from S. Hayashi et al., High-temperature oxidation of Cu-modified Fe–Ni–Cr–Al alloys, in: Y. Murata et al. (Eds.), Proceedings of the First International Conference on Advanced High-Temperature Materials Technology for Sustainable and Reliable Power Engineering, Japan, 2015, pp. 371–374 [75].

4.6 Summary

The first part of this chapter introduces the defect structures of thermal oxides on iron and chromium. The typical thermal oxides formed on iron at temperatures higher than the eutectoid one consist of the oxygen-deficient haematite sitting on the metal-deficient magnetite which sits on the major metal-deficient wüstite. The thermal oxide on chromium is duplex chromia with an internal (resp. external) n-equiaxed (resp. p-columnar) subscales. The Brouwer diagram for chromia formation is also described.

The second part of this chapter reviews the effects of alloying elements on the high temperature oxidation of the chromia-forming stainless steels. Silicon tends to reduce the steel oxidation rate but not in a monotonic manner. Titanium and niobium can help suppress the breakaway oxidation for the austenitic stainless steel since it significantly increases the ratio between the diffusivity of chromium in steel which represents the chromium supply from metal to metal/scale interface and the oxidation parabolic rate constant which represents the chromium consumption rate for oxidation. Titanium can form TiO_2 at the internal metal/scale interface and serves as a mechanical anchor to hold oxide and metal together resulting the improved scale adhesion. The addition of titanium and niobium together into the steel can form TiO_2 but also with Fe_2Nb particles which present between the titania and the metal substrate. This Fe–Nb intermetallic compound can reduce the scale adhesion by reducing the TiO_2 mechanical keying effect. For the AISI 444, Fe–Mo intermetallic compound can also form at the metal/scale interface and consequently reduces the scale adhesion.

The third part of this chapter reviews the high temperature oxidation behaviour of alumina-forming stainless steels. The oxidation rate of this steel is significantly lower than that of the chromia-forming stainless steel. However, the application of this steel is limited especially by the formation of metastable alumina and the limited aluminium content that can be alloyed without degrading the steel mechanical properties. High aluminium content at the surface can delay the transformation of metastable to stable alumina. The presence of Fe_2O_3 on the metal surface can serve as a template for alumina nucleation, thus accelerating the transformation. For the alumina-forming ferritic stainless steel, the addition of chromium can help reduce the critical content of aluminium added to the steel in order to form alumina at high temperatures. However, care must be taken when chromium is added with relatively high content since it can form the brittle chromium-rich bcc phase at 475 °C. Reactive elements can also be added to improve the scale adhesion and reduce the steel oxidation rate. Refractory metals e.g. molybdenum, tungsten and tantalum can be added to the steel to increase its strength. However, the addition of refractory metal like molybdenum can increase the oxidation rate of stainless steel containing reactive elements e.g. zirconium and lanthanum. The alumina-forming austenitic stainless steel has capacity to be used at high temperatures because of its superior oxidation resistance and mechanical properties at high temperatures. However, since the diffusivity of aluminium in austenite is relatively low, the high aluminium content is needed in order to form alumina at high temperatures. This high aluminium content can form B2 phase which can decrease the aluminium content in the matrix and therefore reduces the oxidation performance. The reduced iron content in Ni–20Cr–10Al (at.%) can reduce the volume fraction of B2 phase and therefore gives the lower oxidation rate. Some alumina-forming austenitic grades have been developed e.g. the Fe–17Ni–17Cr–7Al–0.06Zr–0.6Cu (at.%). Addition of copper in the mentioned alloy can reduce the critical content of aluminium to form alumina at high temperatures.

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