Research Article

Li Sun* and Weiping Yan

Analysis of oxide scale thickness and pores position of HCM12A steel in supercritical water

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Abstract: More attention has been paid to the exfoliation of oxide scale on high-temperature heating surface of utility boiler. The oxidation mechanism of HCM12A steel in supercritical water is proposed and the growth of oxide film is simulated. The duplex scale contains an outer magnetite layer and an inner Cr-rich spinel layer. According to the data of Backhaus and Töpfer, the diffusion coefficient values of iron in magnetite layer are discussed and the function of R_V , R_I for oxygen activity can be used for calculation of iron diffusion coefficients in Cr-rich spinel layer. Based on Wagner's oxidation theory, the oxidation rate constants of HCM12A are calculated at 500 and 600°C in supercritical water, compared with experimental data of the relevant literatures. The oxygen activities at the interfaces of alloy/Cr-rich spinel oxide and magnetite/supercritical water are estimated. The simulation results of weight gain are matched with the test data. The iron diffusion mechanisms inside the magnetite layer and the Cr-rich spinel layer are analyzed. The iron diffusion coefficient at the interface of Cr-rich spinel/magnetite is discontinuous, while the oxygen activity is continuous in the whole double layer. The thickness of oxide scale on inner tube walls of the final superheater coils (T91) of a 600 MW supercritical boiler is calculated by using the calculation method provided by the paper. The modeling results, the measured data, and the calculation results by the method are compared. Accurate calculation of the thickness of the inner and outer oxide scales can provide a necessary basis for predicting the stress and exfoliation of oxide scales.

Keywords: supercritical water, HCM12A, thickness, oxide scale, pores

1 Introduction

With the improvement of operation parameters of supercritical and ultra-supercritical boiler power plants, spallation of oxide scale does a lot of harm to some units. In supercritical water environment, oxide scale inevitably generates on high-temperature heating surface of boiler, such as superheater and reheater. In the process of starting and stopping of the unit, scale exfoliation threatens the safety and economy of units. Ferritic–martensitic alloys with excellent properties [1] are often used in high-temperature heating surface of supercritical power generating units. Compared with nickel-based alloys and austenitic stainless steels, the corrosion resistance of ferrite–martensitic steels is lower.

It is generally believed that the reaction of supercritical water with ferrite–martensitic steels results in the formation of double-layer oxide scale, the outer layer of magnetite and the inner layer of Cr-rich spinel with the same thickness. In order to clarify the basic principle of oxidation behavior of ferrite–martensitic steels in supercritical water, researchers have performed a lot of experiments. Yin et al. [2] investigated the corrosion behavior of P92 steel in supercritical water at 500–600°C/25 MPa. The microstructure of the oxide scale was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and the corrosion kinetics of P92 steel in supercritical water were analyzed. The oxide scale is a double-layer structure. The outer oxide layer is Fe_3O_4 phase, and the inner oxide layer is $\text{Fe}_3\text{O}_4/\text{FeCr}_2\text{O}_4$ phases. Geng et al. [3] studied the effect of temperature and flow rate of high-temperature steam on oxidation behavior of T91 steel and the relationship between microstructure and oxidation kinetics of oxidation layer. Xu [4] put forward the “Ecocide Hypothesis” and explained the reason why the oxide film on the steam side is easy to fall off due to oxygenated feed water treatment. The oxygenated treatment of the feed water may damage the environment where the metal oxide film is located. Pores are formed at the interface of the double-layer oxide film due to the evaporation and dissipation of chromium, and the

* **Corresponding author: Li Sun**, Department of Power Engineering, North China Electric Power University, Baoding 071003, China, e-mail: sunli1001315@163.com

Weiping Yan: Department of Power Engineering, North China Electric Power University, Baoding 071003, China

gradual increase of the holes leads to the gradual decrease of the bonding strength of the double-layer oxide film interface. Corrosion tests of two ferritic–martensitic steels, HCM12A and NF616, were carried out in steam and supercritical water at 500°C [5]. The corrosion kinetics of the two alloys are similar, and the corrosion rate in supercritical water is greatly higher than that in steam. In both environments, a double oxide structure is formed on the two steels [5]. Zhong et al. [6] suggested that the weight gain of P92 steel conforms to the power law oxidation kinetics with the increase of oxidation temperature. The activation energy of P92 steel in supercritical water is 174.3 kJ mol^{−1}. The oxide film consists of three layers, the outer layer which is porous hematite, the middle layer which is magnetite, and the inner layer which is chromium and iron-chromium spinel oxides. Tan et al. [7] studied the corrosion behavior of HCM12A and NF616 steels in two different oxidation environments by various characterization techniques. The dissolved oxygen concentration in supercritical water and high-temperature water is less than 25 ppb. The surface morphologies, thickness, and composition of the oxide film were significantly affected by the oxidation temperature and time. The inner spinel layer was found to be porous. The oxidation kinetics and morphologies of oxide film in steam oxidation were usually similar to those formed in air–water vapor environment. Under high temperature and pressure of ultra-supercritical steam cycle, chromium was extensively lost by volatilization. The content of chromium in alloy was closely related to the oxidation rates and morphologies [8]. Martinelli et al. [9] studied the oxidation of Fe–9Cr–1Mo martensitic steel (T91) in static liquid Pb–Bi eutectic alloy. The growth kinetics of double-layer oxide scale were simulated, which was in agreement with the experimental data. Rouillard and Martinelli [10] have suggested that the oxidation of 9Cr1Mo steel in CO₂ at 550°C formed a double-layer oxide film, which consisted of an external layer of magnetite and an internal layer of Cr-rich spinel. The mechanism of void-induced oxidation explained the formation of internal spinel oxide layer and the corrosion kinetics of oxide were simulated.

After long-term service, great changes have taken place in the microstructure of HCM12 steel, and the strength properties at room temperature and high temperature have

decreased. The creep strength loss was estimated to be about 60–70% [11]. The performance test of HCM12A steel in before and after service conditions showed that the measured values of strength properties at room temperature and high temperature were close. So was the hardness value. Long-term service resulted in a relatively slight change of the strength performance value, and the impact strength was reduced by about 50% compared with the condition before using. It is estimated that the creep loss of steel is about 24% [12].

In short, more attention has been paid to lots of experiments in the study on oxidation kinetics of ferritic–martensitic steels, and the kinetic simulation calculation is relatively less focused on. In this study, the oxidation mechanism of HCM12A steel under different environments is presented, the iron diffusion coefficient values in Fe₃O₄ and Fe₂CrO₄ are discussed, and the oxygen activities at the interfaces of steel/Cr-rich spinel oxide and magnetite/supercritical water are estimated. Based on Wagner oxidation theory, the oxidation rate constants of HCM12A (its chemical compositions are listed in Table 1) are calculated at 500 and 600°C in supercritical water, and the weight gain of simulation is compared with experimental results in Bischoff et al. [5,13].

2 Oxidation mechanism

2.1 Summary of previous experimental results

Known from the literatures [2–8], a multilayer oxide scale is formed on ferritic–martensitic steels in supercritical water. The oxidation film growth follows parabolic oxidation kinetics, and the oxide film generally consists of three different layers, namely, a porous surface layer, a dense middle layer, and a bottom diffusion layer. The surface oxide is composed of dense columnar magnetite (Fe₃O₄) particles. The middle oxide consists of Cr-rich spinel oxide Fe_{3–x}Cr_xO₄ equiaxed crystal, in which $x = 0.7–1$ is related to the type of alloy [14]. The results of SEM show that the ratios of Cr and Fe are slightly different in each environment. However, a significant trend

Table 1: Chemical compositions of HCM12A steel (wt%)

Steel	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	N	Nb	Al	V	W
HCM12A	0.11	0.64	0.016	0.002	0.27	0.39	10.83	0.3	1.02	0.063	0.054	0.001	0.19	1.89

of the Fe:Cr ratios is observed in different alloys. The averaged Cr concentrations in the internal oxide of HCM12A are 11.8%. It is observed that the Cr concentrations in the inner layer are relatively close to those in the original alloy substrate, and slight enrichment was observed. Corresponding Fe:Cr:O ratios of inner oxide in HCM12A are 2.1:0.9:4 [14]. So the inner oxide is assumed as a stoichiometry of Fe_2CrO_4 in this study.

2.2 Proposed mechanism in other environments

The oxidation characteristics of different Fe–Cr steels are similar in different environments, such as evaluated temperature steam, CO_2 , and liquid LBE. The “available space model” has become one of the most reliable models to explain the structure of double oxide scale [15]. In this model, Fe atom diffuses outward, and an external oxide film is formed at the oxide/oxidation medium interface, where a large number of vacancies are left. Vacancies condense into voids at the metal/oxide interface, where the oxides decompose and produce micro-channels in the oxide scale. The oxidant passes through micro-channels to metal/oxide interface and a new internal oxide layer is formed. In other words, the internal oxide layer grows inward. Although the oxygen transport is very fast through micro-channels, it is not the growth rate controlling step of internal oxide layer.

3 Modeling of calculation

According to the mass conservation of Fe and Cr, the growth of Cr-rich spinel oxide is related to that of magnetite. Therefore, the oxidation rate of the alloy depends on the diffusion of iron in the oxide layers.

3.1 Assumptions

- Ferrite–martensitic steels form double oxide scale in supercritical water. The external layer is magnetite layer, whose growth is at the interface of supercritical water/magnetite. The internal layer is Cr-rich spinel layer, whose growth is at the interface of alloy/Cr-rich spinel layer. The iron flux through Cr-rich spinel is equal to that through magnetite.

- The oxide film is in a local thermodynamic equilibrium condition.
- The component concentration is fixed at the internal and external interfaces.
- The oxide thickness growth follows parabolic law.
- The deviation stoichiometric ratio of Cr-rich spinel layer composition is very small.
- The influence of cavity and crack is not considered.
- The dissolution of oxide is not considered.

3.2 Formulas

The thickness of growth of the two oxide layers shows a parabolic law over time, and the relations can be described as follows:

$$h_{\text{mag}}^2 = k_{\text{p,mag}} t \quad (1)$$

$$h_{\text{spinel}}^2 = k_{\text{p,spinel}} t \quad (2)$$

where h_{spinel} and h_{mag} are the thicknesses of the Cr-rich spinel layer and the magnetite layer (μm). $k_{\text{p,spinel}}$ and $k_{\text{p,mag}}$ are the oxidation proportionality constants of oxide layers ($\text{cm}^2 \text{s}^{-1}$). t is time (s).

Based on Wagner oxidation theory, the oxidation process of the alloy is controlled by the diffusion of iron in the oxide layer. The oxidation rate constants of the two layers obey the following expression [16]:

$$k_{\text{p,mag}} = \frac{4}{3} \int_{a_{\text{O}_2}^{\text{mag/spinel}}}^{a_{\text{O}_2}^{\text{mag/scw}}} f^{-1} D_{\text{Fe,mag}} d \ln a_{\text{O}_2} \quad (3)$$

$$k_{\text{p,spinel}} = \frac{4}{3} \int_{a_{\text{O}_2}^{\text{steel/spinel}}}^{a_{\text{O}_2}^{\text{mag/spinel}}} f^{-1} D_{\text{Fe,spinel}} d \ln a_{\text{O}_2} \quad (4)$$

where $a_{\text{O}_2}^{\text{steel/spinel}}$, $a_{\text{O}_2}^{\text{mag/spinel}}$, and $a_{\text{O}_2}^{\text{mag/scw}}$ are the oxygen activities at steel/Cr-rich spinel layer interface, Cr-rich spinel layer/magnetite layer interface, and magnetite layer/SCW interface. f is the correlation coefficient of diffusion mechanism and is about 0.5 [16]. $D_{\text{Fe,mag}}$ and $D_{\text{Fe,spinel}}$ are the diffusion coefficients of Fe in Cr-rich spinel and magnetite. $a_{\text{O}_2} = P_{\text{O}_2}/P_{\text{O}_2}^0$, P_{O_2} is the oxygen partial pressure at the interface (atm), $P_{\text{O}_2}^0 = 1 \text{ atm}$.

The iron diffusion coefficient in magnetite and Cr-rich spinel can be showed as a function of oxygen activity by the following formula [17,14]:

$$D_{\text{Fe,mag}} = \frac{A a_{\text{O}_2}^{2/3}}{(1 + 2K_V a_{\text{O}_2}^{2/3})} + B a_{\text{O}_2}^{-2/3} \quad (5)$$

$$D_{\text{Fe,spinel}} = R_V \frac{Aa_{\text{O}_2}^{2/3}}{(1 + 2K_V a_{\text{O}_2}^{2/3})} + R_I Ba_{\text{O}_2}^{-2/3} \quad (6)$$

$$\begin{cases} R_V = D_{\text{spinel,V}}^{\text{topfer}} / D_{\text{mag,V}}^{\text{topfer}} \\ R_I = D_{\text{spinel,I}}^{\text{topfer}} / D_{\text{mag,I}}^{\text{topfer}} \end{cases} \quad (7)$$

where $A = D_V K_V / 12$, $B = 4D_I K_I / 3$, D_V and D_I are self-diffusion coefficients of vacancies and interstitials, and K_V and K_I are the equilibrium constants for the formation of vacancies and interstitials in magnetite. They are functions of temperature [17]. In equation (5), the two terms represent vacancy diffusion and interstitial diffusion of iron, respectively. Both terms are functions of temperature and oxygen activity. Interstitial diffusion of Fe occurs preferentially for low oxygen activity, while iron diffuses through vacancies for high oxygen activity.

It is assumed that the diffusion of iron in magnetite and Cr-rich spinel has the same temperature dependence, R_V and R_I are the ratios between D_V and D_I in Cr-rich spinel and those in magnetite by Töpfer's data [18]. $D_{\text{mag,V}}^{\text{topfer}}$ and $D_{\text{mag,I}}^{\text{topfer}}$ are the partial cation vacancy and interstitial diffusion coefficients in Fe_3O_4 . $D_{\text{spinel,V}}^{\text{topfer}}$ and $D_{\text{spinel,I}}^{\text{topfer}}$ are the partial cation vacancy and interstitial diffusion coefficients in Cr-rich spinel oxide layer.

It is generally believed that the thickness of the consumed alloy is the same as the thickness of the generated Cr-rich spinel layer. The thickness relationship between the two oxide scales can be expressed as follows [14]:

$$h_{\text{spinel}} = \frac{C_{\text{Fe(mag)}}}{C_{\text{Fe(steel)}} - C_{\text{Fe(spinel)}}} h_{\text{mag}} \quad (8)$$

where $C_{\text{Fe(magnetite)}}$, $C_{\text{Fe(spinel)}}$, and $C_{\text{Fe(steel)}}$ are the concentration of Fe in magnetite, spinel, and steel (mol/cm^3), respectively.

3.3 Estimation of iron diffusion coefficients in Fe–Cr spinel and magnetite

Accurate estimation of iron diffusion coefficients in Cr-rich spinel and magnetite is important to the simulation results. The diffusion coefficients of iron in magnetite were given by Töpfer et al. [18] for temperatures at 900 and 1,400°C. The iron diffusion coefficients were proposed by Backhaus-Ricoult and Dieckmann [17], but the coefficients were only for higher temperature conditions. Atkinson et al. [16] confirmed that the iron diffusion coefficients can be estimated to 500°C. The iron diffusion coefficients in Fe_3O_4 and Fe_2CrO_4 were measured at

1,200°C by Töpfer et al. [18], and the iron self-diffusion coefficients at low temperatures can be calculated from the Töpfer's data. The experimental values of diffusion coefficients of iron in Fe_3O_4 and Fe_2CrO_4 at 1,200°C are listed in Table 2.

Linear regression was carried out with data points in Table 2 and the calculation expressions are listed in Table 3. The relation between the expression of R_V and R_I and oxygen activity are derived as:

$$\begin{cases} R_V = 0.49 \\ R_I = 0.0462a_{\text{O}_2}^{0.0078} \end{cases} \quad (9)$$

3.4 Estimation of oxygen activities at interfaces

The oxidation growth rate is connected with the oxygen activities at three interfaces. Furukawa considered that the oxidation growth kinetics do not depend on the properties of the oxidizing medium, but on the oxygen activity in the oxidizing medium [19]. During the oxidation process of T91 in LBE, magnetite and chromium trioxide are formed at first, and then they react together to form iron-chromium spinel layer [9]. Considering the T91/magnetite equilibrium for oxygen activity, the calculated growth rate is close to experimental data. So equilibrium oxygen activity of Fe/magnetite is used as the oxygen activity at steel/Cr-rich spinel interface in this study. The reaction between Fe and H_2O is as follows:

According to Gaskell's data [20], the standard free energy of reaction (10) is listed in the following formula:

$$\Delta G_T = -107,060 + 93.55T \quad (11)$$

Table 2: Logarithm of iron diffusion coefficients measured at 1,200°C at different oxygen activities [18]

$\log_{10} a_{\text{O}_2}$	$\log_{10} D_{\text{Fe,mag}}$	$\log_{10} a_{\text{O}_2}$	$\log_{10} D_{\text{Fe,spinel}}$
−3.23	−7.68	−4.09	−8.45
−4.68	−8.59	−5.54	−9.59
−6.98	−9.3	−6.53	−9.99
−7.84	−8.69	−8.91	−9.70
−8.84	−8.15	−9.55	−9.10
		−10	−8.91
		−10.55	−8.55

Table 3: One-dimensional linear regression equation over logarithm values of iron diffusion coefficients and logarithm values of oxygen activities at 1,200°C, and deterministic coefficient

Oxide	Diffusion via interstitials		Diffusion via vacancies	
	Linear regression equation	Deterministic coefficient	Linear regression equation	Deterministic coefficient
Magnetite	$\log_{10} D_{\text{Fe,mag}} = -0.5893$	0.9975	$\log_{10} D_{\text{Fe,mag}} = 0.6276$	1
	$\log_{10} a_{\text{O}_2} = -13.3433$		$\log_{10} a_{\text{O}_2} = -5.6529$	
Fe–Cr spinel	$\log_{10} D_{\text{Fe,spinel}} = -0.5815$	0.9788	$\log_{10} D_{\text{Fe,spinel}} = -0.6276$	0.9673
	$\log_{10} a_{\text{O}_2} = -14.6786$		$\log_{10} a_{\text{O}_2} = -5.963$	

At 600°C, $\Delta G_T = -25,391$ J, and the equilibrium $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio is 0.03. From dissociation equation, water dissociation reaction rate, Gibbs free energy, and the equivalent oxygen pressure at steel/Cr-rich spinel interface can be evaluated. The equivalent oxygen partial pressure at steel/Cr-rich spinel interface at 500 and 600°C is shown in Table 4.

Cory and Herrington [21] suggested that the steam partial pressure is independent of corrosion rate. The oxygen activity at the interface of magnetite/external layer is not that of oxidizing medium, but that of magnetite/hematite equilibrium. The hematite layer is very thin and will change the oxygen activity at the magnetite/hematite interface.

Fe_2O_3 is formed at the grain boundary of magnetite by reaction (12) at the magnetite/supercritical water interface. Oxygen transports through short-circuit channels and grain boundary, and the oxide layers become thicker. The equivalent oxygen partial pressure at the magnetite/supercritical water interface is not the dissolved oxygen partial pressure, but satisfies the pressure at equilibrium of reaction (12).

According to Gaskell's data [20], the standard free energy of reaction (12) is listed in the following formula:

$$\Delta G_T = -3,440 + 81.7T. \quad (13)$$

Using the methods above, water dissociation reaction rate, Gibbs free energy, and the equivalent oxygen pressure

at magnetite/supercritical water interface can be evaluated. These values at 500 and 600°C are shown in Table 4.

3.5 Thickness of oxide layer and weight gain of the oxide scale

Weight gain of the oxide scales is linear with oxide scale thickness due to the absorption of oxygen. With the increase of exposure time, the internal and external thickness of oxide scale gradually thickens. The thickness relationship between the two oxide layers and weight gain is estimated by the following formula [22]:

$$\Delta w = \rho_{\text{outer}} h_{\text{outer}} \left(\frac{M_{\text{O-outer}}}{M_{\text{Fe}_3\text{O}_4}} \right) + \rho_{\text{inner}} h_{\text{inner}} \left(\frac{M_{\text{O-inner}}}{M_{\text{Fe}_3\text{O}_4 - \text{FeCr}_2\text{O}_4}} \right) \quad (14)$$

where Δw is the amount of absorbed oxygen per unit area in mg cm^{-2} , ρ_{outer} and ρ_{inner} are the external and internal layer density (g cm^{-3}), respectively, h_{outer} and h_{inner} are the external and internal layer thickness, respectively, $M_{\text{O-outer}}$ and $M_{\text{O-inner}}$ are the mole mass of oxygen in external and internal layer, respectively, $M_{\text{Fe}_3\text{O}_4}$ and $M_{\text{Fe}_3\text{O}_4 - \text{FeCr}_2\text{O}_4}$ are the mole mass of external and internal layer, respectively.

Table 4: Thermodynamic data of reaction (10) and (12) at 500 and 600°C

Reaction	Temperature/°C	$\Delta G_T/\text{J}$	$P_{\text{H}_2\text{O}}/P_{\text{H}_2}$	Equivalent P_{O_2} (atm)
$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$	500	-34,746	4.49×10^{-3}	2.01×10^{-29}
	600	-25,391	0.03	3.3×10^{-25}
$2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \rightarrow 3\text{Fe}_2\text{O}_3 + \text{H}_2$	500	59,714	10,846	3.5×10^{-20}
	600	67,884	11,532	2.57×10^{-16}

3.6 Illustration of iron diffusion coefficient, oxygen activity, flux of ion and its divergence as a function of the location (x/X) in the oxide scale

Figure 1 shows a schematic diagram of iron and oxygen diffusion in magnetite layer and Cr-rich spinel layer. During the formation of double oxide scale, iron diffuses inward and oxygen diffuses outward.

The flux of iron in the Cr-rich spinel layer of HCM12A is expressed as [23]:

$$J_{\text{Fe}} = \frac{2C_{\text{Fe(spinel)}}D_{\text{Fe,spinel}}}{2.4} \frac{d \ln a_{\text{O}_2}}{dx} \quad (15)$$

The above formula is integrated through the Cr-rich spinel layer.

$$J_{\text{Fe}}a = \frac{2C_{\text{Fe(spinel)}}}{2.4} \int_{a_{\text{O}_2(\text{I})}}^{a_{\text{O}_2(\text{II})}} D_{\text{Fe,spinel}} d \ln a_{\text{O}_2} \quad (16)$$

The equation (15) is integrated from 0 to x ,

$$J_{\text{Fe}}x = \frac{2C_{\text{Fe(spinel)}}}{2.4} \int_{a_{\text{O}_2(\text{I})}}^{a_{\text{O}_2}} D_{\text{Fe,spinel}} d \ln a_{\text{O}_2} \quad (17)$$

a , b , and X are the thickness of Cr-rich spinel layer, magnetite layer, and whole oxide scale layer, respectively. The oxygen activity and the position (x/X) in the Cr-rich spinel layer have the following relationship:

$$\frac{x}{X} = \frac{\int_{a_{\text{O}_2(\text{I})}}^{a_{\text{O}_2}} D_{\text{Fe,spinel}} d \ln a_{\text{O}_2}}{\int_{a_{\text{O}_2(\text{I})}}^{a_{\text{O}_2(\text{II})}} D_{\text{Fe,spinel}} d \ln a_{\text{O}_2}} \frac{a}{a+b} \quad 0 \leq x \leq a \quad (18)$$

Figure 1: Schematic diagram of iron and oxygen diffusion in magnetite layer and spinel layer

According to the above derivation process, the oxygen activity and the position (x/X) in the magnetite layer have the following relationship:

$$\frac{x}{X} = \frac{\int_{a_{\text{O}_2(\text{II})}}^{a_{\text{O}_2}} D_{\text{Fe,mag}} d \ln a_{\text{O}_2}}{\int_{a_{\text{O}_2(\text{II})}}^{a_{\text{O}_2(\text{III})}} D_{\text{Fe,mag}} d \ln a_{\text{O}_2}} \frac{b}{a+b} + \frac{a}{a+b} \quad (19)$$

$$a \leq x \leq b$$

According to Millot's research [24], the diffusion coefficient of oxygen in Fe_3O_4 at 1,073 and 1,423 K follows an equation of the form:

$$D_{\text{O}} = CP_{\text{O}_2}^{-1/2} + FP_{\text{O}_2}^{1/6} \quad (20)$$

where C and F are the fitting parameters, respectively.

With the data given by Millot, the oxygen diffusion coefficient in magnetite can be estimated to the temperature applied in this study. Because the data of oxygen diffusion coefficient in Cr-rich spinel is not reported, the oxygen diffusion coefficient is assumed to be the same as that in magnetite. The results of extrapolation are in Table 5.

The flux of oxygen in the Cr-rich spinel layer of HCM12A is expressed as [23]:

$$J_{\text{O,spinel}} = -\frac{C_{\text{O(spinel)}}D_{\text{O,spinel}}}{2RT} \frac{d\mu_{\text{O}_2}}{dx} \quad (21)$$

where $C_{\text{O(spinel)}}$ is the concentration of oxygen ion (mol m^{-3}), $D_{\text{O,spinel}}$ the oxygen diffusion coefficient in Fe–Cr spinel layer ($\text{m}^2 \text{s}^{-1}$), and μ_{O_2} the chemical potential of oxygen (J mol^{-1}).

The relation between oxygen chemical potential and oxygen partial pressure is given as:

$$d\mu_{\text{O}_2} = d(\mu_{\text{O}_2}^0 + RT \ln P_{\text{O}_2}) = RT d \ln P_{\text{O}_2} \quad (22)$$

where $\mu_{\text{O}_2}^0$ is the standard chemical potential of oxygen (J mol^{-1}), R gas constant ($\text{J mol}^{-1} \text{K}^{-1}$).

With equations (18), (21), and (22), the flux of oxygen in the Cr-rich spinel layer is derived as follows:

$$J_{\text{O,spinel}} = -\frac{C_{\text{O(spinel)}}D_{\text{O,spinel}}}{2D_{\text{Fe,spinel}}} \frac{\int_{a_{\text{O}_2(\text{I})}}^{a_{\text{O}_2(\text{II})}} D_{\text{Fe,spinel}} d \ln a_{\text{O}_2}}{a} \quad (23)$$

Table 5: The results of extrapolation of parameter C and parameter F

Temperature (°C)	C ($\text{m}^2 \text{s}^{-1} \text{atm}^{1/2}$)	F ($\text{m}^2 \text{s}^{-1} \text{atm}^{-1/6}$)
500	1.74×10^{-36}	3.8×10^{-23}
600	3.07×10^{-32}	5.2×10^{-21}

First order derivative of the variable $J_{O,spinel}$ with respect to the independent variable x , i.e., the divergence of oxygen flux, is derived as:

$$\frac{dJ_{O,spinel}}{dx} = -\frac{C_{O(spinel)}}{2D_{Fe,spinel}} \frac{\left[\int_{a_{O_2(I)}}^{a_{O_2(II)}} D_{Fe,spinel} d \ln a_{O_2} \right]^2}{a^2} \times \frac{\left(-\frac{1}{2}CP_{O_2}^{-3/2} + \frac{1}{6}FP_{O_2}^{-5/6} \right) D_{Fe,spinel} - D_{O,spinel} \left(-\frac{2}{3}R_l Ba_{O_2}^{-5/3} + R_v A \frac{\frac{2}{3}a_{O_2}^{-1/3}(1+2K_v a_{O_2}^{2/3}) - \frac{4}{3}K_v a_{O_2}^{1/3}}{(1+2K_v a_{O_2}^{2/3})^2} \right)}{D_{Fe,spinel}^2} \quad (24)$$

In the same way, the flux of oxygen in the magnetite layer is derived as:

$$J_{O,mag} = -\frac{C_{O(mag)}D_{O,mag}}{2D_{Fe,mag}} \frac{\int_{a_{O_2(II)}}^{a_{O_2(III)}} D_{Fe,mag} d \ln a_{O_2}}{b} \quad (25)$$

The divergence of oxygen flux in magnetite layer is expressed:

$$\frac{dJ_{O,mag}}{dx} = -\frac{C_{O(mag)}}{2D_{Fe,mag}} \frac{\left[\int_{a_{O_2(II)}}^{a_{O_2(III)}} D_{Fe,mag} d \ln a_{O_2} \right]^2}{a^2} \times \frac{\left(-\frac{1}{2}CP_{O_2}^{-3/2} + \frac{1}{6}FP_{O_2}^{-5/6} \right) D_{Fe,mag} - D_{O,mag} \left(-\frac{2}{3}Ba_{O_2}^{-5/3} + A \frac{\frac{2}{3}a_{O_2}^{-1/3}(1+2K_v a_{O_2}^{2/3}) - \frac{4}{3}K_v a_{O_2}^{1/3}}{(1+2K_v a_{O_2}^{2/3})^2} \right)}{D_{Fe,mag}^2} \quad (26)$$

4 Results and analysis

4.1 Iron diffusion coefficient in oxide scale

Using equations (4), (5), (6), and (9), iron diffusion coefficients in Fe_3O_4 and Fe_2CrO_4 are available at 500 and 600°C. The iron diffusion coefficients are presented over oxygen activity at 500 and 600°C, as shown in Figure 2. The vacancy diffusion and interstitial diffusion regions of iron in magnetite at 600°C are shown in the Figure 2.

The kinetics of oxide layer are generally bound up with many factors, such as defect properties, defect concentration, and oxide microstructure [25]. According to Wagner oxidation theory, the oxidation rate constant which depends on the property of the diffusing defect can vary with the oxygen partial pressure. With increasing temperature, the vacancy concentration at the external layer/supercritical water interface is higher than that at the steel/internal layer interface. The external oxygen partial pressure increases and the vacancy concentration increases too. The conversion between a vacancy and an interstitial mechanism depends on the temperature and external oxygen activity. There is a strong correlation between iron self-diffusion coefficient in oxide layer and oxygen activity, and different oxygen activities correspond

to iron diffusion different mechanism in oxide. The iron diffusion under high oxygen activity follows the vacancy mechanism and the interstitial mechanism under low oxygen activity [9].

In fact, the oxygen activity is low at the steel/Cr-rich spinel interface, and iron diffuses via interstitial mechanism. The oxygen activity is high at the magnetite/supercritical water interface and iron diffuses via vacancies mechanism. The oxygen activity at the magnetite/Cr-rich spinel interface

Figure 2: Iron diffusion coefficient in magnetite and Cr-rich spinel over oxygen activity at 500 and 600°C.

needs to be determined by calculation, so it is impossible to predict the diffusion mechanism of the interface. With the increase of temperature, the iron diffusion coefficient and the growth rate of oxide film increase.

4.2 Comparisons between simulation results and experiment results

According to equations (1)–(9) and (14), the simulation of HCM12A in supercritical water at 500 and 600°C under 25 MPa was carried out. The simulation results and experiment results of oxide weight gain are compared in Figure 3.

In ref. [5,13], oxidation tests of HCM12A exposed to SCW at 500 and 600°C, and 25 MPa are performed for oxidation time from 1 to 3,000 h. The dissolved oxygen concentration in supercritical water is less than 20 ppb.

The simulated values of oxidation weight gain of HCM12A at 500 and 600°C are lower than the experimental values. The maximum difference in weight gain at 600°C is 178 mg dm^{-2} , and the equivalent thickness is $12.7 \mu\text{m}$ according to the formula (14). The maximum difference in weight gain at 500°C is 49 mg dm^{-2} , and the equivalent thickness is $3.5 \mu\text{m}$. The reason for the difference may be that the equilibrium oxygen partial pressure of the selected reaction (10) is higher than the actual oxygen partial pressure of the steel/Cr-rich spinel interface at this temperature, or the thermodynamic equilibrium oxygen partial pressure of the reaction (12) is lower than the actual oxygen partial pressure at the magnetite/supercritical water interface.

Over 3,000 h of oxidation, the relative errors between the predicted values and the experimental values of

HCM12A oxidation weight gain in supercritical water at 500 and 600°C are shown in Figure 4.

The relative errors between the simulated values and the experimental values of HCM12A oxidation weight gain at 500 and 600°C are less than 20%, and the calculated values are consistent with the experimental values with increasing time.

Without considering the scale pores, bucking, and peeling, some errors between simulation and experiments of oxidation rate are present.

4.3 Comparison of oxidation rates

From the above relational expression, the oxidation rates of each layer and the overall oxidation rate are calculated and compared with the data in EPRI [26]. These values are shown in Table 6.

The oxidation rates of simulation for HCM12A at 500 and 600°C agree with that of the data in EPRI [26] in the same order. Because of the errors of diffusion coefficients which were estimated to be at low temperature, the oxidation rate of simulation is lower. The oxidation rate of simulation of HCM12A at 600°C is nearly 100 times higher than that at 500°C.

4.4 Analysis of oxygen activities and iron diffusion coefficients in oxide scale

The oxygen partial pressures at the oxide interfaces HCM12A at 500 and 600°C are shown in Table 6. When

Figure 3: Simulation results and experiment results of oxidation weight gain of HCM12A in supercritical water at 500 and 600°C.

Figure 4: Relative errors between the simulated values and the experimental values of HCM12A oxidation weight gain in supercritical water at 500 and 600°C.

Table 6: The oxidation rate of internal and external oxides, k_{mag} , k_{spinel} , the overall oxidation rate, k_{oxide} , and oxygen partial pressure of interfaces

Alloy	Temperature/°C	Oxidation rate constant/(cm ² s ⁻¹)				Oxygen partial pressure at interfaces/atm		
		k_{mag}	k_{spinel}	k_{oxide}	$k_{EPRI[24]}$	$P_{alloy/spinel}$	$P_{spinel/mag}$	$P_{mag/scw}$
HCM12A	500	8.08×10^{-14}	7.03×10^{-14}	3.01×10^{-13}	2.6×10^{-12}	2.01×10^{-29}	1.68×10^{-20}	3.5×10^{-20}
	600	2.16×10^{-12}	1.88×10^{-12}	8.06×10^{-12}	10.1×10^{-12}	3.36×10^{-25}	1.12×10^{-16}	2.57×10^{-16}

HCM12A is oxidized at 600°C, the oxygen activities on both sides of the Cr-rich layer are 3.36×10^{-25} and 1.12×10^{-16} , respectively. From Figure 2, there is a change diffusion of iron via from interstitials to vacancies. The oxygen activities on both sides of the magnetite layer are 1.12×10^{-16} and 2.57×10^{-16} , and iron diffusion follows the vacancy diffusion mechanism. At 500°C, the oxygen activities on both sides of Cr-rich spinel layer are 2.01×10^{-29} and 1.68×10^{-20} , and there is a change diffusion of iron via from interstitials to vacancies. The oxygen activities on both sides of the magnetite layer are 1.68×10^{-20} and 3.5×10^{-20} , and iron diffusion conforms to the vacancy diffusion mechanism.

The normalized position (x/X) is used to express the iron diffusion coefficient in oxide scale of HCM12A in supercritical water for 3,000 h. Figure 5 shows the relationship between the calculated oxygen activities and the normalized position (x/X) in the oxide scale on HCM12A at 600 and 500°C. Figure 6 shows the relationship between the iron diffusion coefficient and the normalized position (x/X) in the oxide scale on HCM12A. The oxygen activity in the oxide scale of HCM12A steel is continuous, but the iron diffusion coefficient at the interface between the internal and external layers is discontinuous.

Figure 5: Model predictions of oxygen activities in oxide scale on HCM12A as a function of normalized position.

It can be seen from Figures 5 and 6 that the oxygen activity in the oxide scale suddenly increases at a certain position, and the iron diffusion coefficient reaches the minimum value. It is possible to form pores at the location of the minimum iron diffusion coefficient. Figure 6 shows relationship between iron diffusion coefficient and normalized position (x/X) in oxide scale on HCM12A at 600 and 500°C. When the normalized position is about 0.05 at 500°C, the iron diffusion coefficient of oxide scale formed on HCM12A reaches the minimum. The higher the experimental temperature, the closer the location of pores to the internal layer/external layer interface.

4.5 Flux of oxygen ion and its divergence in oxide scale

Figures 7–10 show the calculated results in oxide scale formed on HCM12A in supercritical water for 3,000 h at 600 and 500°C. Figure 7 shows the change of the flux of oxygen ion in oxide scale formed on HCM12A at 600 and 500°C over normalized position. The flux of oxygen ion in the double oxide scale is negative. In the case of oxidation of HCM12A at 600°C, the sudden change in the flux of

Figure 6: Relationship between iron diffusion coefficient and normalized position (x/X) in oxide scale on HCM12A.

oxygen ion occurs at the interface between the internal oxide and the external oxide. The flux of oxygen ion sharply increases at a certain position ($x/X = 0.11$) and the normalized position ($x/X = 0.05$) in the magnetite layer during oxidation at 600 and 500°C, respectively.

Figure 8 shows logarithm of negative of flux of oxygen ion in the double oxide scale of HCM12A at 500 and 600°C. The flux of oxygen ion in the double oxide scale is discontinuous at the Cr-rich spinel layer/magnetite layer interface.

Figure 9 shows divergence of oxygen ion flux in the double oxide scale. At 600°C, the divergence of flux of oxygen ion in oxide scale is negative at the range from the substrate/Cr-rich spinel layer interface to the normalized position ($x/X = 0.11$). The divergence of flux of oxygen ion at the Cr-rich spinel layer/magnetite layer interface is discontinuous. Then the divergence of flux of oxygen ion becomes positive from this position to the surface. The drastic change at the normalized position ($x/X = 0.11$) indicates pore formation. At 500°C, divergence of flux of oxygen ion in the double oxide scale is negative at the range from substrate/Cr-rich spinel layer interface to the normalized position ($x/X = 0.05$). The drastic change at the normalized position ($x/X = 0.05$) indicates pore formation. Then divergence of flux of oxygen ion becomes positive from this position to the surface.

Figure 10 shows logarithm of the divergence of flux of oxygen ion in oxide scale on HCM12A at 600 and 500°C over normalized position. Flux of oxygen ion and its divergence in oxide scale are discontinuous at the Cr-rich spinel layer/magnetite layer interface, which indicates pores probably form at this interface.

5 A case verification of a power plant

In the above sections, the oxidation kinetics model of ferritic–martensitic steel was verified by the experimental data of Bischoff [5,13]. In this section, the last stage superheater tube (T91) of a power plant is taken as the research object, and the thickness of oxide scale on the steam side of the last stage superheater is predicted with the above method. The predicted results are compared with the *in situ* measurement data and the results calculated by EPRI's oxidation kinetic parameters.

Since the SG2080/25.4-M969 boiler of a 600 MW supercritical boiler in a power plant was put into operation, oxide scale exfoliation has become a prominent problem. The oxide scale thickness at 13,000, 21,000, 25,000, and 36,000 h at the outlet of the last stage superheater was measured by ultrasonic technique. The range of oxide thickness is shown in Table 7.

According to the above model and relative basic heat transfer theory, the growth model of oxide scale on superheater tubes is put forward by iterative technology [27]. The relevant parameters are from EPRI report [26]. The forecast thickness results of oxide scale on boiler superheater tubes for different service time are given, as shown in Figure 11.

Figure 11 shows the simulation of oxide scale thickness, *in situ* measurement data, and calculation results predicted by a method in ref. [27]. As can be seen from the figure, the predicted results are reliable. The calculated results of this method and the method in ref. [27] are close to the *in situ* measured data. The oxide scale may peel off

Figure 7: Calculated flux of oxygen ion in oxide scale on HCM12A at 500°C (left) and 600°C (right) over normalized position.

Figure 8: Logarithm of negative of the flux of oxygen ion in oxide scale on HCM12A at 500°C (left) and 600°C (right) over normalized position.

Figure 9: Divergence of flux of oxygen ion in oxide scale on HCM12A at 500°C (left) and 600°C (right) over normalized position.

Figure 10: Logarithm of the divergence of flux of oxygen ion in oxide scale formed on HCM12A at 500°C (left) and 600°C (right) over normalized position.

Table 7: *In situ* measurement data and predicted results of oxide scale thickness

Exposure time/h	<i>In situ</i> measurement data of oxide scale thickness/ μm	Predicted results of oxide scale thickness/ μm	Proportional error compared with the maximum value/%
10,000	116–148	172.2	16.4
21,000	188–209	218.9	4.7
25,000	187–225	238.8	6.1
36,000	144–258	286.6	11.1

Figure 11: The oxide scale thickness of last stage superheater tubes for *in situ* measurement data, predicted results, and calculation results according to a method in ref. [27].

during the running of boiler, so the predicted results of the oxide layer thickness are larger than the maximum value of *in situ* measured data.

6 Conclusion

The oxidation kinetics of ferritic–martensitic steel HCM12A in supercritical water at 500 and 600°C can be predicted by simulation. According to the data of Backhaus-Ricoult and Dieckmann [17] and Töpfer et al. [18], the diffusion coefficient of iron in Fe_3O_4 and Fe_2CrO_4 is extrapolated at low temperature. The followings are the major conclusions:

1. The calculated value of oxidation weight gain of HCM12A at 500 and 600°C is close to the experimental value [5,13].
2. The calculated value of oxidation rate is closely related to the value of oxygen partial pressure at the interfaces. The equilibrium oxygen partial pressure of reaction (10) is adopted for the steel/Cr-rich spinel interface, and the equilibrium oxygen partial pressure of reaction

(12) is adopted for the magnetite/supercritical water interface. The calculated rate constant is close to the experimental value. The relative errors between the simulated values and the experimental values of HCM12A oxidation weight gain at 500 and 600°C are less than 20%, and the predicted values are consistent with the experimental data with increasing time. The errors are due to the predicted calculation of iron diffusion coefficient from high temperature to low temperature according to the Töpfer's data [18].

3. According to the data of Backhaus and Töpfer, the diffusion coefficient values of iron in Fe_3O_4 are discussed and R_V , R_I as the function of oxygen activity can be used for calculation of iron diffusion coefficients in Fe_2CrO_4 .
4. The oxygen activity in the oxide scale of HCM12A steel is continuous, but the iron diffusion coefficient at the interface between the internal and external layers is discontinuous. The oxygen activity in the oxide scale suddenly increases at a certain position, and the iron diffusion coefficient reaches the minimum value. It is possible to form pores at the location of the minimum iron diffusion coefficient.
5. This oxidation kinetics model of HCM12A in supercritical water can be applied to other ferritic–martensitic steels.

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