Research Article

Estimation of Oxidation Kinetics and Oxide Scale Void Position of Ferritic-Martensitic Steels in Supercritical Water

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Exfoliation of oxide scales from high-temperature heating surfaces of power boilers threatened the safety of supercritical power generating units. According to available space model, the oxidation kinetics of two ferritic-martensitic steels are developed to predict in supercritical water at 400°C, 500°C, and 600°C. The iron diffusion coefficients in magnetite and Fe-Cr spinel are extrapolated from studies of Backhaus and Töpfer. According to Fe-Cr-O ternary phase diagram, oxygen partial pressure at the steel/Fe-Cr spinel oxide interface is determined. The oxygen partial pressure at the magnetite/supercritical water interface meets the equivalent oxygen partial pressure when system equilibrium has been attained. The relative error between calculated values and experimental values is analyzed and the reasons of error are suggested. The research results show that the results of simulation at 600°C are approximately close to experimental results. The iron diffusion coefficient is discontinuous in the duplex scale of two ferritic-martensitic steels. The simulation results of thicknesses of the oxide scale on tubes (T91) of final superheater of a 600 MW supercritical boiler are compared with field measurement data and calculation results by Adrian's method. The calculated void positions of oxide scales are in good agreement with a cross-sectional SEM image of the oxide layers.

1. Introduction

According to the characteristic of supercritical water [1], supercritical and ultrasupercritical boiler power plants have been constructed for a long time in order to improve efficiency of units in some countries. Under the supercritical water (the critical point of water, 374°C, 22.1 MPa) environment, the corrosion resistance of candidate materials is one of the key requirements for these materials safe application in units. Two ferritic-martensitic steels of candidate structural materials for superheaters and reheaters, such as HCM12A and NF616, have been attracted increasing attention by researchers, because they have good high-temperature strength, high thermal conductivity, creep resistance, and low thermal expansion coefficients [2]. Exfoliation of oxide scales from high-temperature heating surfaces of power boilers threatened the safety of supercritical power generating units, and prediction of oxidation kinetics and void formation of oxide scales are desired.

Generally, good corrosion resistance of the steels with higher Cr contents is presented compared to the steels with lower Cr contents [3, 4]. In order to understand the oxidation mechanism of candidate materials under supercritical water environment, the oxidation tests of ferritic-martensitic steels are performed and the effects of SCW temperature and dissolved oxygen on the oxidation rate are analyzed. The diffusion processes in oxide in terms of diffusion species and mechanisms are determined and the structure of the various oxide phases and their formation are understood [5]. In situ electrical and electrochemical measurements during oxidation of ferritic steel P91 and austenitic steel AISI 316L (NG) in ultrasupercritical water (500–700°C, 30 MPa) have been carried out. The surface and in-depth composition and structure of the oxides formed on ferritic and austenitic steels in ultrasupercritical water are broadly analogous to those obtained by wet air oxidation in the same temperature range [6]. Angell et al. [7] studied the effect of pressure on the steam oxidation of 9Cr-1Mo steels at 500–600°C and the

oxidation of the steels followed a parabolic kinetics with the oxide scale thickness increasing with the increasing pressure. The corrosion of the ferritic-martensitic steel P92 exposed to supercritical water at 550°C under 25 MPa with the dissolved oxygen contents of 100, 300, and 2000 ppb was investigated. The results indicated that the weight gain increased with the dissolved oxygen content [8]. The oxidation behavior of ferritic/martensitic steel HCM12A exposed in SCW at 500°C, 25 MPa, and two levels of oxygen partial pressure were investigated. Oxygen partial pressure effects on oxide structure and porosity in oxide scale are rationalized in terms of thermodynamics and diffusion mechanism. A desirable continuous protective oxide layer structure with limited pores may be obtained by controlling the oxygen partial pressure [9]. Various growth mechanisms of the oxide scale of 9–12% Cr F-M steels exposed to SCW were proposed by Ampornrat and Was [5], Bischoff and Motta [10], and Zhong et al. [11]. The oxide films on F-M steels followed parabolic oxidation kinetics under supercritical water. Microstructure of oxide formed on four F-M steels consisting of two oxide layers and a transition layer. The outer oxide consisted of dense columnar grains of magnetite (Fe_3O_4). The inner oxide consisted of small equiaxed grains of Fe-Cr spinel oxide $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$, where x (0.7–1) depends on alloy type. The transition layer consisted of grain boundary oxides of chromia and chromite and fine oxide grains of a spinel structure precipitated inside laths [5]. Martinelli et al. [12] focused on the growth kinetics simulation of a duplex oxide scale of a Fe-9Cr-1Mo martensitic steel (T91) in static liquid Pb-Bi. The magnetite layer growth is controlled by iron diffusion inside the Fe-Cr spinel and the magnetite lattice. An analytical simulation is matched with the experimental kinetics. Rouillard and Martinelli [13] have suggested that 9Cr-1Mo steel forms in CO_2 at 550°C a duplex oxide layer containing an outer magnetite scale and an inner Fe-Cr rich spinel scale. The inner spinel oxide layer is formed according to a void-induced oxidation mechanism. The kinetics of the total oxide growth are simulated from the proposed oxidation model.

To sum up, the research of oxidation kinetics of two ferritic-martensitic steels is focused on experiments; simulation about oxidation kinetics is relatively few. In the present study, the growth kinetics of oxide films of ferritic-martensitic steel under supercritical water are simulated. Considering the presence of Fe-Cr rich spinel oxide layer, the oxidation rates of magnetite layer and Fe-Cr rich spinel oxide layer are calculated simultaneously. With thermodynamic analysis of reaction of materials and calculation of oxygen activity at the interface, the growth kinetics of the inner layer and the outer layer are simulated. The results of simulation of oxidation of two ferritic-martensitic steels under supercritical water are compared to the experimental data in Tan et al. [14]. An example of one power plant is given. The calculated thickness and quantitative location of voids formation of oxide scale are compared with the experimental results.

2. Assumptions and Formulas of Simulation

Oxidation of different Fe-Cr steels under steam, CO_2 , and LBE leads to the formation of a duplex oxide scale, and

the characteristic of oxide scales is similar. Microstructure of oxide formed on the two steels consisted of two oxide layers, which are a Fe-Cr spinel oxide and a magnetite layer. The oxide thickness ratio is close to 1, and the oxidation rate constant of the two layers follows approximately the parabolic law. The “available space model” is proposed to explain the oxidation mechanism of the duplex oxide scale [15]. In the “available space” model, the thickness ratio between the oxide layers formed is constant with exposure time, because the growth mechanism of both oxide layers is linked. Furthermore, the kinetics of oxidation and especially the growth of the inner layer are not limited by the diffusion of oxygen, which reaches the oxide-metal interface through short-circuits such as microchannels. In general, the original oxide-metal interface corresponds to the outer-inner layer interface during the oxidation of alloys under supercritical water. The outer layer is formed by outward migration of iron while the inner layer is formed by inwards migration of the oxidant. Consequently, the limiting step in this mechanism is the diffusion of iron, which enables the formation of the available space for the oxide to grow in. So the growth of oxide scales is dependant on the diffusion of iron in the double layers.

In order to simulate the oxide growth on ferritic-martensitic steels surface during exposure to supercritical water, the following assumptions are made:

- ① The oxide scale formed on ferritic-martensitic steels in supercritical water contains a dual structure. The outer layer, in contact with supercritical water, is a magnetite layer which grows at the magnetite/supercritical water interface involving an iron diffusion from the steel to this external interface. The inner layer, in contact with the steel, consisted of Fe-Cr spinel layer involving a transport of oxygen from supercritical water to the steel/oxide interface. The iron flux across the Fe-Cr spinel is equal to the iron flux across the magnetite layer. A steady state is reached at the interface between the two oxide layers.
- ② Thermodynamic equilibrium exists at both the steel/oxide and oxide/supercritical water interfaces.
- ③ The composition concentrations are constant at the interfaces.
- ④ The growth of oxide scales follows parabolic laws.
- ⑤ The oxygen activity is constant at interfaces.
- ⑥ The Fe-Cr spinel oxide slightly deviates from the stoichiometry.
- ⑦ The oxide scale is compact and adherent and voids and cracks in the oxide may be neglected.
- ⑧ The dissociation of oxide scales is neglected

Generally, the thickness of consumption of ferritic-martensitic steel is equal to the thickness of the Fe-Cr spinel layer. The relation between the thickness of Fe-Cr spinel layer

and that of the magnetite layer can be described as follows [12]:

$$h_{\text{spinel}} = \frac{C_{\text{Fe(magnetite)}}}{C_{\text{Fe(steel)}} - C_{\text{Fe(spinel)}}} h_{\text{magnetite}}, \quad (1)$$

where h_{spinel} and $h_{\text{magnetite}}$ are the thicknesses of the Fe-Cr spinel layer and the magnetite layer (μm). $C_{\text{Fe(magnetite)}}$, $C_{\text{Fe(spinel)}}$, and $C_{\text{Fe(steel)}}$ are the concentrations of Fe in magnetite, spinel oxide, and steel substrate (mol/cm^3), respectively.

For a given time, the formula of the thickness of oxide scale is as follows:

$$h^2 = k_p t, \quad (2)$$

where h is the thickness of the entire oxide or the thickness of the spinel layer or the thickness of the magnetite layer and k_p is the oxidation rate constant (cm^2/s), respectively. t is time (s).

According to Wagner's theory of oxidation and considering that magnetite is formed by outward migration of Fe ions, the oxidation rate constant of oxide obeys the law as proposed by Atkinson et al. [16]:

$$k_p = \frac{4}{3} \int_{a'_{\text{O}_2}}^{a''_{\text{O}_2}} f^{-1} D^* d \ln a_{\text{O}_2}, \quad (3)$$

where a'_{O_2} and a''_{O_2} are the oxygen activities at oxide/environment interface and steel/oxide interface and f is the correlation factor for the diffusion mechanism and is approximately equal to 0.5. D^* is the tracer diffusion coefficient of Fe in oxide. $a'_{\text{O}_2} = P'_{\text{O}_2}/P^0_{\text{O}_2}$, P'_{O_2} is the oxygen partial pressure (atm) at the interface, $P^0_{\text{O}_2} = 1 \text{ atm}$.

The diffusion coefficient of Fe in oxide is very dependent on different types of defects that are present in the oxide lattice. The concentration of defects is linked to the oxygen activity in oxide scales and the diffusion coefficient of Fe ions is dependent on the oxygen activity in two oxide layers. The diffusion coefficient of Fe ions in magnetite can be expressed by oxygen activity and temperature, and the equation can be written [17]:

$$D_{\text{Fe,mag}} = \frac{A a_{\text{O}_2}^{2/3}}{(1 + 2K_V a_{\text{O}_2}^{2/3})} + B a_{\text{O}_2}^{-2/3}, \quad (4)$$

where $A = D_V K_V / 12$, $B = 4D_I K_I / 3$, D_V and D_I are self-diffusion coefficients of cation vacancies and iron interstitials, and K_V and K_I are the equilibrium constants for the formation of cation vacancies and iron interstitials in magnetite. The first term and the second term as a function of temperature and oxygen activity represent the iron diffusion via vacancies and interstitials. The diffusion of Fe in the outer oxide layer at high-oxygen activities is governed by cation vacancies and cation interstitials at low-oxygen activities.

The diffusion coefficient of Fe in Fe-Cr spinel oxide layer can be expressed by the following relation [13]:

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

$$R_V = \frac{D_{\text{spinel,V}}^{\text{topfer}}}{D_{\text{mag,V}}^{\text{topfer}}}$$

$$R_I = \frac{D_{\text{spinel,I}}^{\text{topfer}}}{D_{\text{mag,I}}^{\text{topfer}}},$$

where $D_{\text{mag,V}}^{\text{topfer}}$ and $D_{\text{mag,I}}^{\text{topfer}}$ are the partial cation diffusion coefficients of the cation diffusion via vacancies (V) and interstitials (I) in Fe_3O_4 . $D_{\text{spinel,V}}^{\text{topfer}}$ and $D_{\text{spinel,I}}^{\text{topfer}}$ are the partial cation diffusion coefficients of the cation diffusion via vacancies (V) and interstitials (I) in Fe-Cr spinel oxide layer. R_V and R_I are the ratios of D_V and D_I of Fe-Cr spinel oxide to that of Fe_3O_4 by Töpfer et al.'s data [18].

According to assumption ①, the iron flux across the Fe-Cr spinel is equal to the iron flux across the magnetite layer. The oxygen activity at the interface of ferritic-martensitic steel/Fe-Cr spinel layer is determined from the oxygen partial pressure of the phase boundary at different temperatures. The oxygen activity at the interface of magnetite/supercritical water is calculated by the thermodynamics equilibrium between Fe_3O_4 and Fe_2O_3 . The oxygen activity at the interface of magnetite/Fe-Cr spinel is unknown. According to (1)–(5), the oxidation rates and thickness of magnetite layer and Fe-Cr spinel layer and the oxygen activity at the interface of magnetite/Fe-Cr spinel can be evaluated.

3. Determination of the Parameters

Two types of ferritic-martensitic steels HCM12A and NF616 were evaluated in this study. The oxidation rates of these steels are calculated in supercritical water at 400°C, 500°C, and 600°C under 25 MPa. A summary of steel composition in weight percent is presented in Table 1 [14].

The densities of F-M steels and magnetite are 7.77 mg/cm^3 and 5.17 mg/cm^3 , respectively. The mole volume of Fe-Cr spinel oxide approximately equals that of magnetite because the lattice parameter of Fe-Cr spinel oxide is close to that of magnetite. According to chemical compositions of the ferritic-martensitic steels HCM12A and NF616 and the densities of scales, the concentrations of Fe in magnetite, spinel oxide, and steel substrate, $C_{\text{Fe(magnetite)}}$, $C_{\text{Fe(steel)}}$, and $C_{\text{Fe(spinel)}}$, are approximately evaluated. The values of $C_{\text{Fe(magnetite)}}/(C_{\text{Fe(steel)}} - C_{\text{Fe(spinel)}})$ for NF616 and HCM12A are 0.985 and 0.932, respectively.

3.1. Determination of Iron Diffusion Coefficient in Magnetite and Fe-Cr Spinel Oxide. The iron diffusion coefficient in magnetite at lower temperatures can be extrapolated from the data of the iron diffusion coefficient for temperatures between 900 and 1400°C, which is given by Backhaus-Ricoult and

TABLE 1: Chemical composition of HCM12A and NF616 (in 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
NF616	0.109	0.45			0.102	0.174	8.82	0.468			0.064		0.194	1.87

Dieckmann [17]. For the iron diffusion coefficient in spinel oxide, the data at 1200°C given by Töfpfer et al. [18] is used and extrapolated towards lower temperature. Assuming the same temperature dependence for iron diffusion in magnetite and in Fe-Cr spinel, the ratio between iron diffusion coefficient in magnetite and in spinel oxide is a function of oxygen activity.

The mean values of the ratio between iron diffusion coefficient via vacancies or interstitials in spinel oxide and in magnetite for different experimental points at 1200°C are calculated, namely, R_V and R_I . For NF616, composition of inner oxide scale is $\text{Fe}_{2.4}\text{Cr}_{0.6}\text{O}_4$ [19], R_V equals 0.644, and R_I equals 0.31. For HCM12A, composition of inner oxide scale is Fe_2CrO_4 [19], R_V equals 0.5, and R_I equals 0.039.

3.2. Estimation of the Oxygen Activities of Magnetite/Supercritical Water Interface and Steel Substrate/Fe-Cr Spinel Interface. Formation of oxide phase depends on the oxygen potential and local chemistry, which can be described by the diffusion path in Fe-Cr-O phase diagrams [19]. The oxygen partial pressure at this interface could be determined from the phase boundary in the predominance diagram. The oxygen partial pressures at steel substrate/Fe-Cr spinel interface are approximately 3×10^{-35} atm, 1×10^{-29} atm, and 2×10^{-25} atm for 400°C, 500°C, and 600°C, respectively.

The real oxygen concentration at the magnetite/atmosphere interface is not the oxygen concentration in air or water. Zurek et al. [20], who studied oxidation of 10% Cr ferritic steel in Ar- H_2O mixture, showed that the oxide scale thickness does not depend on the H_2O content in the gas mixture (Ar-4% H_2O or Ar-50% H_2O) if the oxygen activity is sufficient to allow the thin hematite layer formation. The estimated oxygen partial pressure using Henry's constant of SCW is lower than that of steam. The values also are still quite high compared to a dissociation P_{O_2} of surface oxide phase (magnetite) observed. It can be assumed that the dissolved oxygen was totally removed from water under deaerated condition, and oxygen was miscible under SCW. Therefore, the oxygen partial pressure at specimen surface was very low and resulted from dissociation of water molecules only [19]. The oxidation rate of oxide scale is related to oxygen activity at magnetite/supercritical water. Furukawa et al. [21] suggested that the oxide growth kinetics do not depend on the nature of the oxidizing medium but just on the oxygen activity in the oxidizing medium.

Fe transports through the spinel oxide layer and reacts with H_2O ; the Fe_3O_4 layer becomes thick gradually as exposure time increases. At magnetite/supercritical water interface, Fe_2O_3 is formed through reaction (6) at the grain boundary of magnetite. With outward transport of Fe and inward transport of oxidation species along the oxide grain boundaries and short-circuit paths, both the Fe_3O_4 layer

TABLE 2: Thermodynamic data of oxidation reaction (6) at different temperatures.

Temperature (°C)	ΔG_T (J)	$P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio	Equivalent oxygen partial pressure P_{O_2} (atm)
400	51544	10016	3.46×10^{-25}
500	59714	10846	3.5×10^{-20}
600	67884	11532	2.57×10^{-16}

and Fe-Cr spinel layer became thicker. The real oxygen partial pressure at magnetite/supercritical water interface is not dissolved oxygen partial pressure, but the equivalent oxygen pressure which corresponds to the thermodynamic equilibrium of the following.

Using Gaskell's data [22], the standard free energy for the formation of reaction (6) is given by

$$\Delta G_T = -3440 + 81.7T. \quad (7)$$

At 600°C, $\Delta G_T = 67884$ J, and the equilibrium $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio is 11532. According to dissociation equation, Gibbs free energy, and water dissociation reaction rate, the equivalent oxygen pressure at magnetite/supercritical water interface can be evaluated. The equivalent oxygen partial pressure magnetite/supercritical water interface is as follows at 400°C, 500°C, and 600°C in Table 2.

3.3. Relation between Weight Gain and Thickness of Inner and Outer Layers of Oxide Scale. The weight gain of oxide scales is related to oxide thickness as a linear function because of oxygen absorption during exposure. The density of oxide scales is nearly constant, and the thickness of inner and outer layers of oxide scales is becoming thicker with exposure time increasing. The relation between weight gain and thickness of inner and outer layers of oxide scale was estimated by the following equation [8]:

$$\Delta w = \rho_{\text{outer}} h_{\text{outer}} \left(\frac{4M_o}{M_{\text{Fe}_3\text{O}_4}} \right) + \rho_{\text{inner}} h_{\text{inner}} \left(\frac{4M_o}{M_{\text{Fe}_3\text{O}_4} - \text{FeCr}_2\text{O}_4} \right), \quad (8)$$

where Δw is the amount of absorbed oxygen per unit area in mg/cm^2 , ρ_{outer} and ρ_{inner} are the outer and inner layer density (mg/cm^3), respectively, h_{outer} and h_{inner} are the outer and inner layer thickness (cm), respectively, $4M_o$ are the mole mass of oxygen in oxide layer, and $M_{\text{Fe}_3\text{O}_4}$ and $M_{\text{Fe}_3\text{O}_4} - \text{FeCr}_2\text{O}_4$ are the mole mass of outer and inner layer, respectively.

FIGURE 1: Schematic illustration of diffusion of oxygen and iron in the duplex scale in the magnetite and Fe-Cr spinel formation process.

3.4. The Description of the Oxygen Activity, Iron Diffusion Coefficient, the Flux of Oxide Ion, and Its Divergence in Oxide as a Function of the Location (x/X) in the Duplex Scale. Figure 1 shows a schematic illustration of diffusion of oxygen and iron in the duplex scale formed on ferritic-martensitic steel. The iron migrates outward during the growth of the duplex scale, while the oxidant migrates inwards.

The flux of iron in the Fe-Cr spinel layer formed on NF616 is described as [23]

$$J_{Fe} = \frac{2C_{Fe(spinel)}D_{Fe,spinel}}{2.4} \frac{d \ln a_{O_2}}{dx}. \quad (9)$$

The integration is performed over the entire Fe-Cr spinel layer.

$$J_{Fe}a = \frac{2C_{Fe(spinel)}}{2.4} \int_{a_{O_2(I)}}^{a_{O_2(II)}} D_{Fe,spinel} d \ln a_{O_2}. \quad (10)$$

Equation (9) is integrated from $x = 0$ to $x = x$:

$$J_{Fe}x = \frac{2C_{Fe(spinel)}}{2.4} \int_{a_{O_2(I)}}^{a_{O_2}} D_{Fe,spinel} d \ln a_{O_2}. \quad (11)$$

The values of a , b , and X are the thickness of Fe-Cr spinel layer, magnetite layer, and entire duplex scale layer, respectively; that is, $a + b = X$. The relationship between the oxygen activity and the location (x/X) in the Fe-Cr spinel layer can be derived as follows:

$$\frac{x}{X} = \frac{\int_{a_{O_2(I)}}^{a_{O_2}} D_{Fe,spinel} d \ln a_{O_2}}{\int_{a_{O_2(I)}}^{a_{O_2(II)}} D_{Fe,spinel} d \ln a_{O_2}} \frac{a}{a+b} \quad 0 \leq x \leq a. \quad (12)$$

According to assumption ①, the iron flux across the Fe-Cr spinel is equal to the iron flux across the magnetite layer.

With the above method, the relationship between the oxygen activity and the location (x/X) in the magnetite layer can be expressed as

$$\frac{x}{X} = \frac{\int_{a_{O_2(II)}}^{a_{O_2}} D_{Fe,mag} d \ln a_{O_2}}{\int_{a_{O_2(II)}}^{a_{O_2(III)}} D_{Fe,mag} d \ln a_{O_2}} \frac{b}{a+b} + \frac{a}{a+b} \quad (13)$$

$$a \leq x \leq b.$$

3.5. Process of the Calculation. The oxygen partial pressure at the magnetite/SCW interface could be determined from Fe-Cr-O phase diagrams [19]. The oxygen partial pressure at the steel/Fe-Cr spinel interface can be calculated by the thermodynamical equilibrium of reaction (6) from Section 3.2.

The oxygen activities (i.e., $a_{O_2(I)}$ and $a_{O_2(III)}$) at the magnetite/SCW and the steel/Fe-Cr spinel interfaces are known. The only unknown variable is thus the oxygen activity ($a_{O_2(II)}$) at the Fe-Cr spinel/magnetite interface. With (1)–(5), the oxygen activity ($a_{O_2(II)}$) is quantified. Then the magnetite layer oxidation rate, k_{mag} , and the Fe-Cr spinel layer oxidation rate, k_{spinel} , can be evaluated. And the thickness (h_{mag}) of the magnetite layer and the thickness (h_{spinel}) of Fe-Cr spinel layer can be calculated also. The weight gain of oxide scale can be estimated by thickness of inner and outer layers of oxide scale with (7).

4. Results and Discussion

4.1. Iron Diffusion Coefficient in Magnetite and Fe-Cr Spinel Oxide. According to (4) and (5), the iron diffusion coefficient in magnetite and Fe-Cr spinel oxide is evaluated at different temperatures. The relation between oxygen activity and iron diffusion coefficient in the oxides for HCM12A and NF616 is expressed as a function of logarithm of diffusion coefficients and logarithm of oxygen activity on Figure 2. The different kinds of diffusion regimes of iron diffusion coefficient in magnetite, vacancy, and interstitial are also specified on Figure 2.

The oxide growth kinetics depend on the oxygen activity in the interfaces. The self-iron diffusion has a strong dependence on the oxygen activity in the oxide. The value of the oxygen activity fixes the iron diffusion mechanism, which can follow either a vacancy mechanism for high-oxygen activities or an interstitial mechanism for low-oxygen activities.

In fact, the oxygen activity is low and the iron diffuses through the interstitial mechanism at the steel/oxide interface. The iron diffusion coefficient jumps from the Fe-Cr spinel to the magnetite one at the Fe-Cr spinel/magnetite interface. The diffusion mechanism at this site is still not predictable because the oxygen activity is needed to be calculated. The oxygen activity is high and the iron diffuses through the vacancy mechanism at the magnetite/supercritical interface.

4.2. Comparison between Simulation and Experiments of Oxide Weight Gain and Error Analysis. Using (1)–(5), (8), the simulation is performed for HCM12A and NF616 exposed to

FIGURE 2: Iron diffusion coefficient of the duplex scale formed on HCM12A (a) and NF616 (b) as a function of oxygen activity in supercritical water at different temperatures.

supercritical water at 400°C, 500°C, and 600°C under 25 MPa. The comparison between simulation and experiments of oxide weight gain are presented in Figure 3.

In [14], tests are performed on NF616 exposed to a SCW at 400, 500, and 600°C and 25 MPa with an oxygen concentration of less than 25 ppb in weight for time periods from 1 to 3000 h.

For HCM12A, the simulation of oxidation weight gain is lower than experimental value at 500°C and 600°C. The maximum difference between calculation and experiment of weight gain at 600°C is 104 mg/dm² and is equivalent to thickness of about 7.5 μm according to formula (8). The maximum difference between calculation and experiment of weight gain at 500°C is 181 mg/dm² and is equivalent to thickness of about 13 μm. The maximum difference between calculation and experiment of weight gain at 400°C is 2 mg/dm² and is equivalent to thickness of about 1.57 μm.

For NF616, the simulation of oxidation weight gain is higher than the experimental values at 600°C. The maximum difference between calculation and experiment of weight gain at 600°C for 3000 hours is 306 mg/dm² and is equivalent to thickness of about 22 μm. The reason is that the hematite phase was not detected in outer oxide layer [8], and the selective thermodynamic equilibrium oxygen partial pressure of reaction (6) is larger than actual pressure during calculation. The simulation of oxidation weight gain is lower than the experimental values at 500°C. The maximum difference between calculation and experiment of weight gain for 3000-hour exposure is 76 mg/dm² and is equivalent to thickness of about 5.4 μm.

For 3000 hours of exposure, relative error of simulated weight gain by oxidation of HCM12A and NF616 in supercritical water at different temperatures compared to the experiments is shown in Figure 4.

The relative error of oxide weight gain between simulation and experiments on NF616 at 500°C and 600°C and HCM12A at 600°C is less than 20%, and the calculated values are close to experimental values. The relative error of oxide weight gain between simulation and experiments on HCM12A at 400°C and 500°C is above 40%.

4.3. Comparison and Analysis of Oxidation Rates. In [24], the temperature dependence of the parabolic rate constant is given by

$$k_{\text{EPRI}} = 2 \cdot A \cdot \exp\left(-\frac{Q}{RT}\right), \quad (14)$$

where Q is the activation energy for the rate-controlling process, T is the metal temperature (absolute), A is the Arrhenius constant, and R is the Universal Gas Constant. The oxidation parameters used for alloy NF616 are $Q = 5.13 \times 10^{10} \mu\text{m}^2/\text{hr}$ and $A = 169 \text{ kJ/mole}$. The oxidation parameters used for alloy HCM12A are $Q = 5.6 \times 10^4 \mu\text{m}^2/\text{hr}$ and $A = 75 \text{ kJ/mole}$.

According to the above equations, the oxidation rate of inner layer and outer layer and the global oxidation rate which is compared to the data in [24] are evaluated. These values are presented in Table 3.

FIGURE 3: Experimental weight gain by oxidation of HCM12A (a) and NF616 (b) in supercritical water at different temperatures compared to the simulation.

FIGURE 4: Relative error of simulated weight gain by oxidation of HCM12A (a) and NF616 (b) in supercritical water at different temperatures compared to the experiments.

The simulation of oxidation rates for NF616 and HCM12A at 550°C and 600°C are the same order of magnitude as one of the data in [24].

The simulation of oxidation rate for NF616 at 600°C is nearly two orders of magnitude higher than that at 500°C, while the simulation of oxidation rate for HCM12A at 600°C

is nearly one order of magnitude higher than that at 500°C. The oxidation rate of Fe-Cr spinel layer is lower than that of magnetite layer because of the presence of Cr in Fe-Cr spinel layer. HCM12A with higher Cr contents show superior oxidation resistance as compared to NF616 with lower Cr contents at the same temperature.

TABLE 3: Oxidation rate of inner and outer layer oxides, k_{mag} and k_{spinel} , the global oxidation rate, k_{oxide} , and oxygen partial pressure of interfaces.

Steel	Temperature ($^{\circ}\text{C}$)	oxidation rate (cm^2/s)				Oxygen partial pressure at interfaces (atm)		
		k_{mag}	k_{spinel}	k_{oxide}	k_{EPRI} [24]	$P_{\text{alloy/spinel}}$	$P_{\text{spinel/mag}}$	$P_{\text{mag/scw}}$
NF616	500	1.66×10^{-13}	1.61×10^{-13}	6.54×10^{-13}	—	1×10^{-29}	3.3×10^{-21}	3.5×10^{-20}
	550	8.84×10^{-13}	8.57×10^{-13}	3.45×10^{-11}	5.35×10^{-12}	3.5×10^{-27}	3.97×10^{-19}	3.9×10^{-18}
	600	6.33×10^{-12}	6.15×10^{-12}	2.5×10^{-11}	2.22×10^{-11}	2×10^{-25}	1.41×10^{-23}	2.57×10^{-16}
HCM12A	400	1.3×10^{-15}	1.13×10^{-15}	4.85×10^{-15}	—	3×10^{-35}	1.66×10^{-25}	3.46×10^{-25}
	500	8.85×10^{-14}	7.7×10^{-14}	3.3×10^{-13}	—	1×10^{-29}	1.53×10^{-20}	3.5×10^{-20}
	550	4.8×10^{-13}	4.17×10^{-13}	1.8×10^{-12}	5.4×10^{-12}	3.5×10^{-27}	1.7×10^{-18}	3.9×10^{-18}
	600	2.46×10^{-12}	2.14×10^{-12}	9.2×10^{-12}	10.1×10^{-12}	2×10^{-25}	9.59×10^{-17}	2.57×10^{-16}

4.4. *The Distribution of Oxygen Activities and Iron Diffusion Coefficient in Duplex Oxide Scale.* The oxygen partial pressures at interfaces of oxidation of HCM12A and NF616 at different temperatures are listed in Table 4. For the oxidation of NF616 at 600°C , the oxygen activity in the Fe-Cr spinel layer evolves from 2×10^{-25} to 1.41×10^{-23} , and the diffusion process follows an interstitial mechanism; the oxygen activity in the magnetite layer evolves from 1.41×10^{-23} to 2.57×10^{-16} , and the diffusion process varies from an interstitial mechanism to a vacancy mechanism. For the oxidation of HCM12A at 600°C , the oxygen activity in the Fe-Cr spinel layer evolves from 2×10^{-25} to 9.59×10^{-17} , and the diffusion process varies from an interstitial mechanism to a vacancy mechanism; the oxygen activity in the magnetite layer evolves from 9.59×10^{-17} to 2.57×10^{-16} , and the diffusion process follows a vacancy mechanism.

The iron diffusion coefficient in the duplex scale of two ferritic-martensitic steels exposed to supercritical water for 3000 h is expressed as a function of normalized position (x/X). Figure 5 shows calculations of the oxygen activity distribution in the Fe-Cr spinel layer and the magnetite scale formed on NF616 and HCM12A at 600°C and 500°C . Figure 6 shows the iron diffusion coefficient distribution along thickness direction of the duplex scale formed on NF616 and HCM12A at 600°C and 500°C . In the duplex scale of two ferritic-martensitic steels, the oxygen activity is continuous, while the iron diffusion coefficient is discontinuous at the inner layer/outer layer interface.

For the oxidation of NF616 at 600°C , the oxygen activity drastically increases at the normalized position ($x/X = 0.6$), while iron diffusion coefficient becomes minimum. For the oxidation of HCM12A at 600°C , the oxygen activity drastically increases at the normalized position ($x/X = 0.2$), while iron diffusion coefficient becomes minimum. There are two diffusion mechanisms of iron in the oxide, including interstitial mechanism and vacancy mechanism. When the vacancy concentration in oxide is high enough, the vacancies may collapse into voids. From Figure 2, with increasing of the oxygen activity, the diffusion mechanism changes from interstitial to vacancy. The vacancy diffusion mode starts to act a primary role at the location of the minimum diffusion coefficient of iron. So void is expected to form at the location of the minimum iron diffusion coefficient.

As shown in Figure 6, the iron diffusion coefficient in the Fe-Cr spinel layer on NF616 is higher than that in the Fe-Cr spinel layer on HCM12A, while the iron diffusion coefficient in the magnetite layer on NF616 is close to that in the magnetite layer on HCM12A. The oxygen partial pressure at the inner layer/outer layer interface formed on NF616 and HCM12A at 500°C is 3.3×10^{-21} and 1.53×10^{-20} , respectively (Table 4). The normalized position of the minimum iron diffusion coefficient in the duplex scale is about 0.4 and 0.1 (Figure 6), so the location of void formation in duplex scale formed on NF616 is close to the inner layer/outer layer interface compared to that formed on HCM12A. Similar result, which is that the minimum iron diffusion coefficient of low-oxygen exposed sample occurs at the location closer to the surface compared to high-oxygen exposed sample, has been reported in HCM12A oxidized in supercritical water [25].

4.5. *Model Validation of an Example of One Power Plant.* In the previous section, the model of oxidation kinetics of the ferritic-martensitic steel is validated with experimental data of Tan et al. [14]. In this section, the tubes (T91 steel) of the final superheater in one power plant are selected as research objects, and the thickness of steam side oxide scales of the final superheater is estimated by the above method. The simulation results are compared with field measurement data of the oxide scale thickness and calculation results by the EPRI's oxidation kinetics parameters.

Since its service, exfoliation of the oxide scale has become an acute problem in a 600 MW supercritical unit of one power plant, whose boiler type is SG2080/25.4-M969. The main thermodynamic parameters of the boiler, for example, calculation, are listed in Table 4. The thicknesses of oxide scales of the outlet part of the final superheater are measured by ultrasonic technology after 13000 h, 21000 h, 25000 h, and 36000 h periods of service. The range of values of thickness of oxide scales is listed in Table 5.

In order to verify the simulation of oxidation kinetics of ferritic-martensitic steels, an oxide scale growth model of superheater tubes is established. The empirical formula correlating scale thickness with the simulation oxidation rates is combined to the heat transfer theory. The model involves forced convections on the inner surface due to the

TABLE 4: Main thermodynamic parameters of a boiler, for example, calculation.

Item	Unit	BRL	BMCR
Superheated steam mass flow	t/h	1979	2080
Pressure of superheated steam outlet	MPa	25.28	25.4
Temperature of superheated steam outlet	°C	571	571
Reheated steam flow	t/h	1638	1764
Pressure of reheated steam inlet	MPa	4.38	4.6
Pressure of reheated steam outlet	MPa	3.28	3.66
Temperature of reheated steam inlet	°C	313	318
Temperature of reheated steam outlet	°C	569	569

FIGURE 5: The calculation oxygen activity in the duplex scale formed on NF616 (a) and HCM12A (b) as a function of normalized position.

FIGURE 6: The diffusion coefficient of iron in the duplex scale formed on NF616 (a) and HCM12A (b) as a function of the normalized position.

TABLE 5: Comparison between field measurement data and simulation results of oxide scale thickness.

Exposure time/h	Field measurement data of oxide scale thickness/ μm	Simulation results of oxide scale thickness/ μm	Relative error compared to the maximum value/%
10000	116–148	177.5	19.9
21000	188–209	225.6	7.9
25000	187–225	246.1	9.4
36000	144–258	295.4	14.5

FIGURE 7: Comparison of the thickness of oxide scale of final superheater tubes during the oxidation of T91 for different exposure time among field measurement data, simulation results, and calculation results according to Sabau and Wright's method [26].

turbulent flow of steam and on the outer surface due to cross flow of the hot flue gas over ash tubes. The oxidation rates of ferritic-martensitic steels at different temperatures are calculated and carried out by a quadratic multinomial fitting. An iterative procedure is used to determine scale thickness as both temperature and time increase [26]. The results are presented in Figure 7.

Based on the parabolic law of high-temperature oxidation, Arrhenius equation, and related basic theories of heat transfer, an oxide scale growth model of boiler superheater tubes is proposed through iterative technique [26]. Related parameters are from the EPRI report [24]. According to this algorithm, the calculation results of oxide scale thickness of boiler superheater tubes for different exposure time are presented in Figure 7.

Figure 7 shows the predicted oxide scale thickness, the field measurement data, and calculated results by Sabau and Wright's method. From this figure, it can be concluded that the prediction results are credible. The calculation results of

FIGURE 8: A cross-sectional SEM image of the oxide layer formed on T91 used in a superheater tube for 25000 hours.

this method and Sabau and Wright's method are comparatively close to field measurement data. Because exfoliation of oxide scales probably emerged during the operation of the unit, the maximum value of the field measurement data is lower than calculation results of oxide thickness of boiler superheater tubes. The parameters in Adrian's iterative method are extrapolated from field measurement data, so the calculated results are closer to the actual experimental data.

To verify the location of voids, the scanning electron microscope image of the oxide layer formed on T91 used in a superheater tube for 25000 hours is captured and shown in Figure 8. The experimental thickness of oxide scale is $225.34 \mu\text{m}$, and the distance is $125.2 \mu\text{m}$ from the steel/Fe-Cr spinel interface to the location of void formation. The calculated quantitative location of voids formation ($x/X = 0.52$) is in good agreement with the experimental result ($x/X = 0.56$) with minor difference.

5. Conclusion

Based on available space model, the oxidation kinetics of two ferritic-martensitic steels are developed to predict in supercritical water at 400°C , 500°C , and 600°C . The iron diffusion coefficients in magnetite and Fe-Cr spinel, which are extrapolated from studies of Backhaus-Ricoult and Dieckmann [17] and Töpfer et al. [18], are used for calculation of oxidation kinetics of steels under supercritical water environment. The main conclusions are as follows.

- (i) The simulation of oxidation of NF616 at 500°C and 600°C and HCM12A at 600°C is approximately close to the experimental weight gain during the oxidation of NF616 and HCM12A in supercritical water at 400 – 600°C [14], which proves the validity of the simulation assumptions.
- (ii) The simulation value of the oxidation rate depends on oxygen partial pressure at the steel/spinel interface and magnetite/supercritical water interface. The equilibrium oxygen partial pressure of reaction (6) is used as oxygen partial pressure at magnetite/supercritical water interface, and the results of calculation are in agreement with the experimental weight gain.

- (iii) The relative error of oxide weight gain between simulation and experiments of HCM12A at 400°C and 500°C is above 40%, and the reason is that magnetite/supercritical water oxygen partial pressure is not the equilibrium oxygen partial pressure of reaction (6) or probably the error of diffusion coefficient when it extrapolated from high temperature to low temperature according to Töpfer et al.'s data [18].
- (iv) In the duplex scale of two ferritic-martensitic steels, the oxygen activity is continuous, while the iron diffusion coefficient is discontinuous at the inner layer/outer layer interface. The oxygen activity drastically increases at one normalized position (x/X), while iron diffusion coefficient becomes minimum. Void is expected to form at the location of the minimum iron diffusion coefficient.
- (v) At the same oxidation temperature, the iron diffusion coefficient in the Fe-Cr spinel layer on NF616 is higher than that in the Fe-Cr spinel layer on HCM12A, while the iron diffusion coefficient in the magnetite layer on NF616 is close to that in the magnetite layer on HCM12A.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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