Oxidation model for construction materials in supercritical water—Estimation of kinetic and transport parameters

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ABSTRACT

An upgraded model was employed to obtain estimates of kinetic parameters of oxidation of stainless steel Sanicro 28 (UNS N08028) and nickel-based alloy 690 (UNS N06690) in supercritical water at 650 °C/25 MPa up to 2000 h. In the present approach, it is assumed that the growth of the outer layer is governed by the transport of cations through the inner layer via an interstitialcy mechanism. The model is able to reproduce quantitatively the depth profiles of constituent elements oxide layer, as well as in the transition layer situated between the inner layer and the bulk alloy.

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1. Introduction

As part of the Generation IV International Forum (GIF), the Supercritical Water Reactor (SCWR) is a promising design operating at high core outlet temperature (between 500 and 650 °C depending on the design) above the critical point of water (374 °C, 22.1 MPa). The use of a single phase coolant eliminates the need for components such as steam generators, steam separators, dryers, recirculation and jet pumps, and thus simplifies the design leading to much higher efficiency (ca. 45% vs. 33% of current Light Water Reactors) [1–3]. Supercritical Water (SCW) is expected to be more aggressive toward structural materials also in fossil fuel power plants [4–6]. The performance of materials used as thin-walled components in this environment continues to be a challenge [7,8]. The conditions in an SCWR core are much harsher compared to conventional water cooled reactor (WCR) core conditions where the temperature can be as high as 800 °C at the surface of the fuel cladding. The very high temperature in combination with irradiation is very different from those found in current WCR or in fossil-fired SCW power plants. Thus, the design for the SCWR calls for advanced cladding materials with high irradiation and corrosion resistance, as well as mechanical properties at high temperature [9,10].

The main candidate construction materials considered for the SCWR are austenitic steels and nickel-based alloys, as well as ferritic/martensitic and oxide dispersion strengthened (ODS) steels. ODS steels are extensively investigated nowadays in view of their resistance to irradiation embrittlement and their high temperature strength [11,12]. However, data of corrosion resistance properties of prospective construction materials in SCW are limited, especially at higher temperatures (>600 °C) [1–4,13–18]. Thus in order to achieve lower oxidation rates, further structural material performance data have to be obtained and models need to be developed and validated for more demanding operating conditions.

In order to understand the fundamentals of oxidation behavior of materials under high temperature and pressure conditions, a combination of ex-situ analytical studies of the oxide film forming processes and modeling approaches to those processes is needed. The overall objective of our long-term program [19–23] is to assess the general corrosion mechanism using a deterministic model of the oxide layers. The first step toward the estimation of the kinetic and transport parameters of individual metallic constituents was to test the validity of a quantitative model for in-depth composition of oxides on ferritic and austenitic steels in light water reaction coolants extended recently to supercritical water environments [21].

The overall goal of the present paper is to estimate the parameters of inner and outer layer growth on construction materials exposed to SCW environments using an upgrade of a model used to predict the growth of ferritic and austenitic steels in high-temperature water conditions that has already been proposed and

Nomenclature

c_j	$(j = $ Fe, Cr, Ni, Mn, Si, Cu, Nb, Ti, Mo) molar concentration (mol cm^{-3})
D_{eff}	Effective diffusion coefficient (cm^2 s^{-1})
D_{gb}	Grain boundary diffusion coefficient (cm^2 s^{-1})
D_{gi}	Grain interior diffusion coefficient (cm^2 s^{-1})
D_{I}	Diffusion coefficient of interstitial cations in the inner layer (cm^2 s^{-1})
$D_{j\text{DL}}$	$(j = $ Fe, Cr, Ni, Mn, Si, Cu, Nb, Ti, Mo) diffusion coefficient in the transition layer between the inner oxide and the bulk alloy (cm^2 s^{-1})
D_{O}	Diffusion coefficient of oxygen vacancies in the inner layer (cm^2 s^{-1})
D_{V}	Diffusion coefficient of cation vacancies in the inner layer (cm^2 s^{-1})
$\vec{E}$	Electric field strength in the inner layer (V cm^{-1})
f_{gb}	Fraction of grain boundaries
J_{I}	Flux of interstitial cations in the inner layer (mol cm^{-2} s^{-1})
$k_{1,j}$	$(j = $ Fe, Ni, Mn, Si, Cu, Nb, Ti, Mo) rate constant of interstitial cation formation at the alloy/inner layer interface (mol cm^{-2} s^{-1})
$k_{1\text{Cr}}$	Rate constant of consumption of chromium ion vacancies at the alloy/inner oxide interface (cm s^{-1})
k_2	Rate constant of oxide formation via oxidation and injection of oxygen vacancies (mol cm^{-2} s^{-1})
$k_{3\text{Cr}}$	Rate constant of injection of chromium vacancies in the inner layer (mol cm^{-2} s^{-1})
$k_{3\text{i},j}$	$(j = $ Fe, Cr, Ni, Mn, Si, Cu, Nb, Ti, Mo) rate constant of formation of outer layer at the inner layer/outer layer interface (cm s^{-1})
k_4	Rate constant of oxygen incorporation via consumption of oxygen vacancies at the inner layer/outer layer interface (cm s^{-1})
L_{in}	Thickness of the inner layer of oxide (cm)
$L_{\text{in}}(t=0)$	Initial thickness of the inner layer of oxide (cm)
L_{out}	Thickness of the outer layer of oxide (cm)
L_{D}	Penetration depth of the diffusion layer (cm)
$V_{\text{m,MO}}$	Molar volume of the phase in the oxide layer (cm^3 mol^{-1})
X	Nominal valence of a cation in the oxide
y_j	$(j = $ Fe, Cr, Ni, Mn, Si, Cu, Ti, Nb, Mo) atomic fraction of a cation in the oxide
$y_{j,\text{a}}$	$(j = $ Fe, Cr, Ni, Mn, Si, Cu, Ti, Nb, Mo) atomic fraction of metallic constituent at the diffusion layer/inner layer interface
$y_{j,\text{DL}}$	$(j = $ Fe, Cr, Ni, Mn, Si, Cu, Ti, Nb, Mo) atomic fraction of metallic constituent in the bulk alloy underneath the diffusion layer
$\alpha 2$	Transfer coefficient of the oxidation reaction at the alloy/film interface
δ_{gb}	Grain boundary width (cm)
Φ	Grain size of the oxide (cm)
Φ_0	Grain size of the native oxide (cm)

tested [21,24–28]. As a result of the calculations, kinetics of inner and outer growth and oxide layer restructuring, as well as modifications in the diffusion layer between the bulk substrate and the inner layer will be obtained and the model will be verified and validated for two austenitic materials – Sanicro 28 (UNS N08028) and nickel-based alloy 690 (UNS N06690).

2. Model description

2.1. Main processes

According to the Mixed Conduction model (MCM) for passive films on construction materials and its adaptations to corrosion layers in high-temperature water environments [21,24–28], the growth of the inner layer of oxide proceeds via generation of normal cation positions and oxygen vacancies at the interface with the alloy:

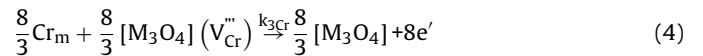$$3M_m \xrightarrow{k_2} [M_3O_4](4V_O^{\bullet\bullet}) + 8e' \tag{1}$$

The Kroger–Vink notation is used throughout the present paper. The oxygen vacancies are then transported by diffusion-migration to the film/electrolyte interface where they are consumed by reaction with oxygen.

$$[M_3O_4]\left(4V_O^{\bullet\bullet}\right) + 4H_2O \xrightarrow{k_4} [M_3O_4] + 8H^+ \tag{2}$$
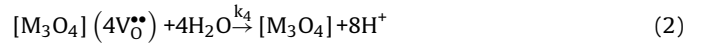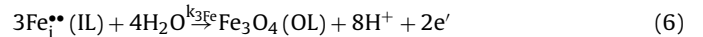
In writing these reactions, it is assumed that the inner layer has a spinel structure. This assumption is verified a posteriori using X-ray diffraction analysis.

In parallel to that reaction, for materials with high chromium content, film growth can proceed via chromium cation transmission through the inner layer, involving generation of cation vacancies at the outer interface, their transport and consumption at the inner interface.

$$4H_2O \xrightarrow{k_{3Cr}} [M_3O_4]\frac{8}{3}\left(V_{Cr}'''\right) + 8H^+ \tag{3}$$

$$\frac{8}{3}Cr_m + \frac{8}{3}[M_3O_4]\left(V_{Cr}'''\right) \xrightarrow{k_{3Cr}} \frac{8}{3}[M_3O_4] + 8e' \tag{4}$$

The other alloy constituents, e.g., Fe, Ni, Mn, Mo, etc., are assumed to be transferred through the inner layer via generation, transport and consumption of interstitial cations exchanged with normal cation sub-lattice sites (the so-called interstitialcy mechanism). An example using Fe is given below:

$$Fe \xrightarrow{k_{1Fe}} Fe_i^{\bullet\bullet} (IL) + v_m + 2e' \tag{5}$$

$$3Fe_i^{\bullet\bullet} (IL) + 4H_2O \xrightarrow{k_{3Fe}} Fe_3O_4 (OL) + 8H^+ + 2e' \tag{6}$$

where v_m is a vacancy in the metal. In the present treatment, it is assumed that the growth of the outer layer of oxide is due to direct reaction of interstitial cations with water and/or oxygen at the inner layer/outer layer interface layer, as recently proposed by Sloppy et al. [29] for the growth of bi-layer oxides on tantalum at ambient temperature and others [4,30,31] for SCW oxidation of stainless steels. A simplified picture of the processes described above is presented in Fig. 1.

In order for film growth to take place under free corrosion conditions, a transfer of electrons through the inner layer to couple the oxidation of metal constituents with the reduction of water and dissolved oxygen is needed. Within the framework of the MCM, it is assumed that ionic point defects play the role of electron donors or acceptors [24], the electronic conduction being coupled to the transport of ionic defects via the so-called resonance (band-to-band) tunneling mechanism that is to certain extent analogous to polaron hopping [24,25,32]. The present model approach does not consider electronic conduction to be a rate-limiting step since in-situ electric resistance and electrochemical impedance measurements during oxidation of ferritic and austenitic steels in supercritical water in the temperature range between 500 and 700 °C have demonstrated that the specific conductivity of the oxide layer is comparable to that on pure iron, i.e. it is a good electronic conductor [19]. No such measurements are available for nickel-based alloys in SCW, however, electric resistance measurements in subcritical water and high-temperature aqueous