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Estimation of kinetic parameters of the corrosion layer constituents on steels in supercritical water coolant conditions

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ABSTRACT

A model for the distribution of individual metallic constituents (Fe, Cr, Ni, Mn) in the corrosion layers on steels in supercritical water is proposed. A detailed description of the model concept and the calculation procedure is given. To verify and validate the model, its predictions are quantitatively compared to depth profiles of the oxides on ferritic–martensitic and austenitic steels as estimated by surface analytical techniques. Estimates of kinetic and transport parameters of the oxidation process for ferritic–martensitic and austenitic stainless steels in supercritical water are obtained. Predictive calculations of the growth kinetics of the respective oxides are presented and discussed.

1. Introduction

The development of Generation-IV nuclear reactor technology is revolutionary in many respects and innovative steps in plant and system design will be taken during the concept elaboration and implementation. The development strategy of supercritical water cooled reactors (SCWRs) assumes that most required components can be derived from future LWRs or from supercritical fossil fired power plants. However, several basic processes seem to be fundamentally different from the NPPs in commercial use today (Generations II–III), involving, for example, new types of moderator and coolant, materials and neutron energy spectra ranging from thermal to fast. Thus, a range of technical issues have to be solved before the implementation stage of the Generation-IV technology [1,2].

The efficiency of coal fired/nuclear power plants depends mainly on the coolant temperature and pressure. Thus oxidation resistance is one of the limiting factors in the service life of the designed Generation-IV nuclear system components. As temperature increases, oxidation rate is generally higher and its reduction is one of the main targets of many ongoing or planned experimental studies nowadays.

To achieve lower oxidation rates, material performance data have to be obtained and models need to be developed and demonstrated for the more demanding operating conditions. Thus, in order to understand the fundamentals of oxidation behaviour of the candidate materials under very high temperature and pressure conditions, a combination of in situ investigations and ex situ analytical studies of the oxide film forming processes with modelling approaches to those processes is needed.

A number of ferritic–martensitic (F/M) steels, austenitic stainless steels and nickel-based alloys have been studied as candidates for structural materials in SCWR applications [3–25]. Test temperatures have reached up to 700 °C with dissolved oxygen content varied from <5 ppb to 8 ppm. As a result, it has been found that corrosion resistance under SCWR conditions is influenced by alloy type, initial surface state of the samples and temperature, as well as water chemistry conditions. At the moment, there is no report of a commercially available material with low Ni content which would sustain long-term exposure under SCW conditions at temperatures higher than 600 °C. The most promising materials for in-core applications seem to be certain modifications of austenitic alloy 310, as well as high Cr oxide dispersion strengthened (ODS) steels.

In order to understand the behaviour of the metal/oxide film/coolant system on a theoretical level and to develop predictive tools for the corrosion behaviour, physical–chemical modelling is of utmost importance. The overall objective of the present work is to assess the general corrosion mechanism of candidate materials using a deterministic model of the oxide films formed. In this paper, the first step towards the estimation of the kinetic and transport parameters of individual metallic constituents is made by testing the validity of a quantitative model for in-depth composition of oxides on stainless steels in LWRs proposed earlier by some of us [26–30]. To achieve that, a calculation procedure is developed and verified using data on the in-depth chemical composition of ferritic–martensitic and austenitic steel published both by us and other authors [3,10,21,24].

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Nomenclature

α_1	transfer coefficient of the oxidation reactions at the alloy/film interface
c_j	(j = Fe, Cr, Ni, Mn) molar concentration (mol cm^{-3})
$D_{i,j}$	(j = Fe, Cr, Ni, Mn) diffusion coefficient of cations in the inner layer (cm^2 s^{-1})
$D_{o,j}$	(i = Fe, Cr, Ni, Mn) diffusion coefficient of cations in the outer layer (cm^2 s^{-1})
$\vec{E}$	electric field strength (V cm^{-1})
J_j	(j = Fe, Cr, Ni, Mn) flux of cations in the inner layer (mol cm^{-2} s^{-1})
$J_{diff,Fe}$	flux of iron in the outer layer (mol cm^{-2} s^{-1})
$k_{1,j}$	(j = Fe, Cr, Ni, Mn) rate constant of oxidation at the alloy/inner layer interface (mol cm^{-2} s^{-1})
$k_{3,j}$	(j = Fe, Cr, Ni, Mn) rate constant of dissolution/redeposition at the inner layer/outer layer interface (cm s^{-1})
$k_{OL,j}$	(j = Fe, Cr, Ni, Mn) rate constant of dissolution/redeposition at the outer layer/coolant interface (cm s^{-1})
L_i	thickness of the inner layer of oxide (cm)
$L_i(t = 0)$	initial thickness of the inner layer of oxide (cm)
L_o	thickness of the outer layer of oxide (cm)
n_j	(j = Fe, Cr, Ni, Mn) amount of a metallic constituent in the oxide (mol)
n_{TOT}	total amount of metallic constituents (mol)
$V_{m,MO}$	molar volume of the phase in the oxide layer (cm^3 mol^{-1})
X	nominal valency of Fe cation in the oxide
y_j	(j = Fe, Cr, Ni, Mn) molar fraction of a cation in the oxide
$y_{j,a}$	(j = Fe, Cr, Ni, Mn) atomic fraction of metallic constituent in the alloy

2. Theoretical background

According to the Point defect model (PDM) [31,32] and the Mixed conduction model (MCM) for passive oxide films on construction materials [33–35], the growth of the inner, compact layer of oxide proceeds via generation of normal cation positions and oxygen vacancies at the interface with the alloy. The oxygen vacancies are then transported by diffusion-migration to the film/electrolyte interface where they are consumed by reaction with adsorbed water. In parallel to that process, metal cation transmission through the layer, involving either the generation of cation vacancies at the outer interface, their transport and consumption at the inner interface, or generation, transport and consumption of interstitial cations, is also expected to occur. Due to the low solubility of the constituent metals in the SCW coolant, the dissolved cations are expected to mainly redeposit and form the outer layer, or react directly with water and/or oxygen at the inner layer/water interface in the pores of the outer layer to form the outer part of the oxide.

For the sake of simplicity, at this point the types of ionic point defects (vacancies and/or interstitial cations) via which the respective metallic constituents are transported through the inner part of the corrosion layer are not distinguished (Fig. 1). Thus, the reaction rate constant at the alloy/inner layer interface for Fe (k_{1Fe}), for example, can be regarded as the sum of the reaction rate constants of oxidation of Fe producing interstitial cations, normal Fe positions and oxygen vacancies and consuming cation vacancies. The same applies for the case of other oxide constituents, such as Cr, Ni and Mn. On the other hand, the diffusion coefficients $D_{i,Cr}$, $D_{i,Fe}$, $D_{i,Ni}$ and $D_{i,Mn}$ can be regarded as characterising the overall transport of cations through the inner layer resulting either from its growth via generation, transport and consumption of oxygen vacancies or the transfer of such cations through the inner layer via a vacancy or interstitial mechanism.

In order film growth to proceed under free corrosion conditions, a transfer of electrons through the inner layer to couple the oxidation of metal constituents with the cathodic partial reaction of reduction of water is needed. Within the PDM and the MCM, it is assumed that ionic point defects play the role of electron donors [30,31], the electronic conduction being coupled to the transport of ionic defects. The present model approach does not consider electronic conduction to be a rate-limiting step, however, since in situ electric resistance and electrochemical impedance measurements during oxidation of ferritic and austenitic steels in supercritical water have demonstrated that the specific conductivity of the oxide layer is close to that on magnetite, i.e. it is a good electronic conductor [24].

In the case of SCW, in analogy to what has been found in subcritical LWR coolants at temperatures above 150 °C [34,35], the large number of defects in the oxide films at high

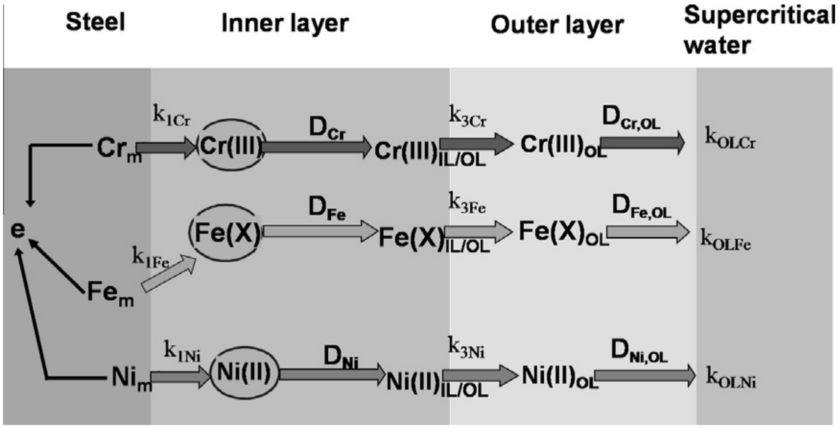

Fig. 1. A simplified scheme of the growth of the inner and outer layers of the film formed on a structural material according to the proposed approach. For details see text.