



Corrosion of nickel-base alloys in primary medium of pressurized water reactors: New insights on the oxide growth mechanisms and kinetic modelling



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ARTICLE INFO

Article history:

Received 12 March 2015

Received in revised form 31 August 2015

Accepted 2 September 2015

Available online 8 September 2015

Keywords:

A. Nickel alloys
C. Reactor conditions
C. Oxidation
B. Modelling studies
C. Kinetic parameters

ABSTRACT

The generalised corrosion of Ni-base alloys exposed to pressurized water reactors primary coolant leads both to the growth of a protective oxide scale and to the release of cations. Based on experimental results previously published, a mechanistic description of this phenomenon is proposed. Then, from a simplified view of these mechanisms, a kinetic model is proposed, focusing on the link between the alloy subsurface defects density and the shape of oxidation kinetic curves. Comparing calculated curves and experimental data shows this first approach is promising. Nevertheless a better knowledge of some kinetic parameters is necessary to improve the model.

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1. Introduction

The environmental degradation of Ni-base alloys (such as Alloys 600 or 690) exposed to pressurized water reactors (PWR) primary coolant (i.e. aqueous solution [$\text{pH} \approx 7$] at high temperature [about 285–325 °C] and high pressure [about 155 bar] containing typically H_3BO_3 , LiOH and dissolved hydrogen) has been largely studied in the past sixty years for at least two practical reasons: (i) the contamination of the primary circuit is mainly the consequence of the Ni cations release, resulting from the generalised corrosion of steam generator (SG) components made of Ni-base alloys and (ii) the stress corrosion cracking (SCC) of SG tubes made of Alloy 600 eventually results in a decrease of the SG thermal exchange efficiency (after the plugging of the cracked tubes). In these phenomena, the oxide film which grows at the alloy surface plays a key role.

The oxide scale formed during the corrosion of Ni-base alloys in simulated PWR primary media (hydrogenated or at least deaerated) is generally described as having a multilayered structure [1–11]. The external part of this scale is mainly composed of scattered Fe and Ni rich crystals [2,4–6,11] whereas the inner one is protective

and rich in chromium [1–7,9,11]. By combining results obtained in previous works by scanning electron microscopy (SEM) [6], transmission electron microscopy (TEM) [6,12], photoelectrochemical techniques (PEC) [13] and X-ray photoelectron spectroscopy (XPS) [14], a more detailed description of this oxide layer can be proposed, as schematised in Fig. 1. This scale can be divided in two major parts. The external layer, made of nickel ferrite ($\text{Ni}_{(1-2)}\text{Fe}_{(2+2)}\text{O}_4$) and nickel hydroxide, is discontinuous and non-protective. The internal one is mainly composed of a continuous layer of mixed iron and nickel chromite ($\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$). Furthermore, nodules of Cr_2O_3 , with a size about 5 nm, are uniformly distributed at the interface between the mixed chromite layer and the alloy.

In parallel with the characterization works mentioned above, experimental studies have been conducted in order to better understand (i) the formation mechanisms of the external layer [6,14] and (ii) the growth mechanisms of the internal one, particularly in terms of growth location [15], semiconducting [13] and oxygen diffusion [15,16] properties.

Therefore, the first part of the paper presents a review of these two sets of data, in order to propose in a second part a scheme of elementary steps depicting mechanisms which govern the oxide scale growth resulting from Ni-base alloys immersion in simulated PWR primary media. The formulation of such mechanisms, describ-

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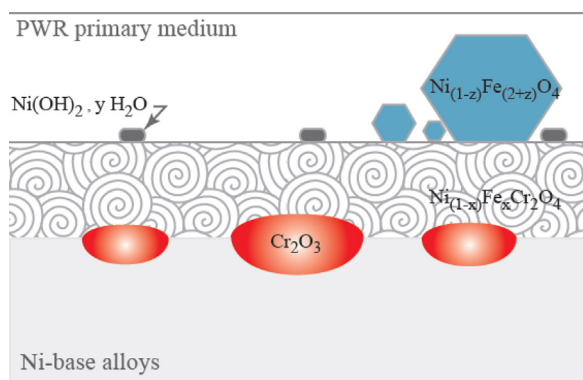


Fig. 1. Schematic view of the oxide scale that forms during the exposure of Ni-base alloys in simulated PWR primary medium [6,12–14].

ing interfacial reactions and species fluxes through the oxide scale, is a first step in the course of oxide growth kinetic modelling.

The third part of the paper is then focused on the modelling of the protective scale growth kinetics. Since the pioneer work of Wagner [17] which has led to the proposition of the parabolic law for describing the growth kinetics of oxide scale when a diffusion process through this scale is the rate-controlling step, many models have been proposed to take into account various aspects of this intricate problem. Some of them focus for example on (i) the roles of the electric field and electric properties of the film [18–23], (ii) the dissolution of the film when it is formed in aqueous environments [19–21], (iii) the growth of multilayered scales [22–26] sometimes implying transport through interconnecting pores [24,26], (iv) the alloy depletion of its most-reactive element [27], (v) the effect of a short-circuit diffusion network and its evolution with time [28] or (vi) a mixed kinetic control involving an interfacial reaction as well as a diffusion process across the oxide scale [29]. However, to the authors' knowledge, no model has been published to describe the evolution of oxide growth kinetics with respect to the alloy subsurface defect density (such as near surface cold-work) although this parameter was known to affect the oxidation rate [16,30].

In the particular case of Alloy 690 corrosion in simulated PWR primary media, it was shown that the kinetics of protective scale growth [16] and cation release [31] strongly depend on the density of structural defects (resulting from cold-work and Xe implantation respectively in Refs. [31] and [16]) existing prior to the corrosion tests and located in the alloy subsurface region. For an increasing defect density, structural modifications of the protective oxide layer, characterized by increasing Cr_2O_3 nodule and chromite grain boundaries network densities [12,16], have been evidenced. Lefaix-Jeuland et al. [16] have discussed, in terms of rate-controlling step, the link between the structural modifications mentioned above and changes in the shape of growth kinetic curves.

On the basis of a simplified view of mechanisms reported in the second part of the paper, a model is proposed in order to formalise the link between the alloy subsurface defect density and the shape of oxide growth kinetic curves. The results obtained are compared to published experimental data and the limits of this first approach are discussed, particularly in terms of relevant kinetic parameters and developments needed to achieve a more robust and quantitative model.

2. Oxide scale growth: a literature review

In this section, a review of results reported in the literature about the mechanisms governing the oxide scale growth during the exposure of Ni-base alloys to PWR primary media is made in order to achieve their decomposition into elementary steps in Section 3.

As shown in Fig. 1, the internal part of the oxide scale is composed of a continuous layer of $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ and of Cr_2O_3 nodules uniformly dispersed along the oxide/alloy interface. Contrary to what has been sometimes exhibited from oxygenated primary water exposures [32], TEM characterisations of the internal oxide scale formed during the immersion of Ni-base alloys to conventional PWR primary media (i.e. containing dissolved hydrogen) have not evidenced any porosity in this scale [3–6,12]. For that reason, all transport through the internal oxide scale is supposed to occur by solid state processes.

Experiments involving gold markers and isotopically labelled oxygen have shown that the formation of the internal scale results from anionic diffusion along short-circuits network such as grain boundaries [15,16]. Photoelectrochemical studies [13] have also demonstrated that $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ and Cr_2O_3 formed during Ni-base alloys corrosion in PWR primary conditions are n-type semiconductors. At this stage, the point defects responsible for their growths seem to be in substitution in the anionic sublattice. In the reactions reported below (see Section 3), these point defects are assumed to be oxygen vacancies although some experimental evidence for the coexistence of oxygen vacancies and hydroxide ions has recently been reported [33].

If anionic diffusion seems to be responsible for the growth of the internal oxide scale, the formation of the external one, as well as the release of cations into the primary fluid, need Fe and Ni diffusion through the internal layer. Considering semiconducting properties of both $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ and Cr_2O_3 , the diffusion of Fe and Ni cations takes place via interstitial sites, in the cationic sublattices. As it has been shown that oxygen diffusion through the protective scale involves a short-circuits network [15], it is assumed that is also the case for cations diffusion.

Had Cr_2O_3 formed a continuous layer, the elements summarized above would have been sufficient to describe the growth mechanisms of the internal part of the scale. However, because of the occurrence of Cr_2O_3 as nodules dispersed along the chromite/alloy interface, nucleation processes must be considered in addition to anionic growth processes, in order to well describe the formation of chromia. As mentioned previously by Lefaix-Jeuland et al. [16], the presence of Cr_2O_3 nodules also affects $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ growth mechanisms. Two distinct interfaces must be considered to achieve the description of the $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ growth (see Fig. 1): the chromite/alloy interface and the chromite/chromia one. Two parallel mechanisms may thus contribute to the chromite formation. On the one hand, the growth of $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ at the chromite/alloy interface involves inward anionic diffusion and direct consumption of the alloy. On the other hand, the chromite growth at the chromite/chromia interface seems to proceed by chromia consumption, which involves (i) oxygen diffusion through $\text{Ni}_{(1-x)}\text{Fe}_x\text{Cr}_2\text{O}_4$ and (ii) Fe and Ni diffusion through Cr_2O_3 .

The growth of a Cr-rich protective oxide scale implies preferential oxidation of Cr, which is coherent with the appearance, often reported in the literature, of a Cr-depleted zone in the alloy immediately beneath the oxide layer [3–5,16]. Moreover, considering that the diffusion of Fe and Ni as interstitial cations through the Cr-rich scale can lead to metal vacancies appearance in the underlying alloy, the transport of Cr through the Cr-depleted zone seems to be promoted by counter diffusion of metal vacancies.

The external part of the oxide scale is made of $\text{Ni}_{(1-z)}\text{Fe}_{(2+z)}\text{O}_4$ crystals and nickel hydroxide, which can be partially hydrated, forming globular-looking aggregates with dimensions on the order of few nanometres [6].

It has been shown that the formation of nickel ferrite crystals results from precipitation phenomena, because (i) they can appear on Fe-free alloy [6] and (ii) the amount of $\text{Ni}_{(1-z)}\text{Fe}_{(2+z)}\text{O}_4$ formed depends on media saturation [6,14]. The roles of substrate (i) subsurface defects and (ii) crystalline orientation on the preferential

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