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Nanostructure and local properties of oxide layers grown on stainless steel in simulated pressurized water reactor environment

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ABSTRACT

The morphology and local electrical resistance of duplex oxide films formed on 316L stainless steel at 325 °C in simulated primary coolant of pressurized water reactor have been investigated at the nanometre scale with Conductive Atomic Force Microscopy. The electrical resistance varies over ~1 order of magnitude for most oxide grains and over 2–3 orders of magnitude locally at grains and grain boundaries. This is rationalized in terms of local variation of the composition and thus resistivity of the mixed Fe(II)–Cr(III) barrier inner layer of the oxide films with grain boundaries of the outer layer possibly promoting Cr(III) enrichment.

1. Introduction

One of the major materials challenge for continued safe, reliable and cost-effective utilisation of water-cooled nuclear reactors for electricity production is to develop the understanding of the fundamental mechanisms responsible for corrosion and stress corrosion cracking degradation of austenitic steels and nickel base alloys [1]. Austenitic 304L and 316L stainless steels owe their high corrosion resistance in water to the formation of a continuous oxide layer, the passive film, only a few nanometre thick at ambient temperature, strongly enriched in Cr(III) and separating and protecting the alloy from the corrosive medium [2,3]. In high temperature aqueous solutions, the slow growing oxide films, also enriched in Cr(III), are thicker and provide corrosion protection [4–16].

Numerous studies of oxide films formed on austenitic stainless steels in high temperature aqueous solutions focused on the thickness, composition, morphology and crystallographic structure of the oxide films [4–16]. Others addressed the influence of cold work and Cr concentration on the stress corrosion cracking (SCC) behaviour [17,18]. Most studies reported the observation of a duplex oxide layer with a Fe-rich outer layer and a Cr-rich inner layer [4–14]. A three-layer structure has also been mentioned [15]. Three models have been proposed to explain the growth of a duplex oxide layer: (i) solid state growth for the internal layer and precipitation of metal ions released from the corroding surface for the outer layer [5,6], (ii) solid state growth for both layers [4], and (iii) metal dissolution and oxide precipitation for both layers [19].

The outer oxide layer is composed of magnetite (Fe_3O_4) [9,12] or iron–nickel spinel oxide [5–8,15]. For the Cr-rich inner layer, composition and phase are subject to controversy. Some studies mention a chromium oxide hexagonal (corundum) phase [13,14,16] while others tend to favour chromium spinel oxides (fcc phase) [4–6,8,9,11,12], or even a mixture of both [15]. In addition, Ni enrichment at the metal/oxide interface has been reported [9,12–14,20]. The amorphous or crystalline character of the oxide layers seems dependent on oxidation time. For 304L surfaces exposed to 300 °C water at pH = 10 for more than 5 h (5–576 h) [7], a double layer oxide film with an outer crystalline layer overlying an amorphous inner layer was reported. However, for 316L surfaces oxidized in simulated pressurized water reactor (PWR) environment [12], the inner layer structure evolves from amorphous, for oxidation times of 1 min, to nano-crystalline at 2 min and mono-crystalline after 5 h. The outer layer is composed of crystallites after 1 min. This study also revealed an epitaxial relationship between inner oxide layer and underlying alloy.

Over the last two decades Conductive Atomic Force Microscopy (C-AFM) has been applied for characterisation of the electrical transport properties of a large variety of materials or devices, including integrated circuits [21], self-assembled monolayers [22], biomolecules [23,24], carbon nanotubes [25,26] or oxide nanorods [27]. Application to oxide films has been reported in a few cases only [28–31]. For cobalt surfaces subjected to atmospheric corrosion for 3 months, the variations of current measured between tip and sample under constant applied bias voltage were larger than one order of magnitude and assigned to local thickness variations of

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the ultrathin (2 ± 1 nm) oxide film [28]. Also on Co, a similar result was found for an ultrathin (1.2 ± 0.1 nm) Al_2O_3 film [29]. For polycrystalline titanium, the conductivity of the air-formed native oxide film was found to be at least 200 times higher above underlying Ti grain boundaries than above Ti grains [30], and the authors concluded to a highly non-stoichiometric and defective oxide layer formed above the substrate grain boundaries. For duplex stainless steel, the air-formed oxide film was found to be more electrically heterogeneous and conductive on ferrite grains than on austenite grains and the difference was observed to be attenuated with aging in ambient conditions [31].

It should be noted that in most cases, current detection with C-AFM is performed using a transimpedance amplifier [32], which limits the current range and makes the technique useless when a large dynamic range covering several orders of magnitude is necessary. This problem was resolved by inserting an additional circuit with a logarithmic current amplifier in a commercial atomic force microscope, the so-called "Resiscope" extension [33–35].

In the present work, AFM and C-AFM (Resiscope) have been applied to study oxide films formed by interaction of 316L stainless steel with simulated PWR primary water at 325 °C. To our knowledge, no investigation with C-AFM has been performed on stainless steels or alloys oxidized in high temperature water and this study will be the first of this kind. The objective was to characterise the nanometre scale morphology of the oxide films providing corrosion resistance to the substrate and to get new knowledge on the relationship between nanostructure and local properties (i.e. electrical resistance) of oxide films of such complex composition, which is a key aspect for local failure of the protection. In the following, we first discuss the morphology of the oxide film measured by AFM and then the relationship with the electrical resistance measured by C-AFM (Resiscope).

2. Experimental

2.1. Sample preparation

Surface preparation and exposure at 325 °C of the specimens to simulated PWR primary water was performed at EDF Les Renardières. The substrate material was 316L stainless steel composed (wt%) of Cr (17.6), Ni (12), Mo (2.39), Mn (1.78), Si (0.59), N (0.08), C (0.028) and Fe (balance) and heat treated at 1000 °C for 10 min. All disk samples were (i) mechanically polished down to 1 μm with diamond paste, then (ii) mechano-chemically polished with colloidal silica to get a mirror finish, and finally (iii) ion etched with Ar ions (4.5 keV, 70°) to remove the chemically affected layer. Oxidation was performed in a micro-autoclave connected to a loop both entirely made of titanium in order to avoid Fe, Cr, and Ni contamination. The solution simulating the PWR primary coolant was pure water with 1000 ppm boron, 2 ppm lithium and 30 cc/kg-H_2O dissolved hydrogen [12,36]. Oxidation temperature was 325 °C. Samples oxidized for 2 and 10 min (AFM/C-AFM) and 100 h (AFM) were analysed for this work. Oxidation times between 10 min and 100 h were discarded due to the very slow increase of the oxide film thickness (see below).

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) were coupled to analyse chemical composition and architecture of the grown oxide layers [37]. ToF-SIMS depth profiling revealed a non-homogenous in-depth composition consistent with a duplex structure of the oxide films. XPS showed that the outer layer was mostly Fe(II)–Fe(III). Nearly no Mo(VI) was found in this outer part. The inner layer was rich in Cr(III) and contained Fe(II)–Fe(III). Mo(VI) was enriched in this inner part. The total thickness d of the oxide film increased from ∼5 to ∼12 and ∼20 nm for oxidation times of 2, 10 and 6000 min, respectively, with respective contributions of the inner and outer parts as listed in Table 1. Nickel was only measured in significant amounts in the oxide film for oxidation time of 6000 min. Ni(II) was then measured and probably present as nickel hydroxide and as spinel ($Ni_xFe_{1-x}Cr_2O_4$) in the outer and inner parts, respectively. According to previous work [12], the outer layer becomes heterogeneous after 5 h of oxidation in simulated PWR environment.

2.2. Scanning probe microscopy measurements

An Agilent 5500 AFM/SPM microscope operated in intermittent contact (tapping®) mode was used for analysing the nanostructure of the oxide films. In this mode, the cantilever supporting the tip oscillates at its resonant frequency and the feedback loop maintains the oscillation amplitude constant (constant tip-sample interaction) by adjusting the vertical position z of the scanner at each (x, y) data point of the scan. The tip used was made of n-doped silicon and had a nominal radius of curvature less than 10 nm.

The same microscope was coupled to a Resiscope module (Resiscope II) for analysing the local electrical properties. The Resiscope covers a wide resistance range from 10^2 to 10^{12} Ω (current range from 1 mA to 100 fA). In this case, the sample surface is scanned in contact mode by a conductive tip and a constant sample-to-tip bias voltage is applied. During the surface scan, the deflection of the cantilever supporting the tip is maintained at a constant value by a feedback loop that continuously adjusts the cantilever height in order to follow the topography at constant applied force. Recording the current at each point where height data are acquired leads to simultaneous mapping of the topography and electrical resistance. The conductive tip-cantilever system (APPNANO: ANSCM Series) was made of n-doped silicon coated by a thin layer of Pt-20Ir and the nominal tip apex radius was less than 30 nm. Reproducibility of the measurements has been tested and validated by repeating several measurements on different samples areas (at least 3) and by changing the sample bias voltage for the C-AFM measurements.

Considering an elastic mechanical contact between conductive tip and sample, which is reasonable because quite low contact forces were applied in our Resiscope measurements, the radius a of the contact area can be estimated by using Hertz' law [33,38]

$$a = \left(\frac{3FR_t}{4E^*}\right)^{1/3} \quad \text{with} \quad \frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \qquad (1)$$

where F denotes the contact force, R_t the tip radius, and ν_1, ν_2, E_1 and E_2 the Poisson's ratios and Young's moduli of the probe (material 1) and sample (material 2), respectively. Taking values

Table 1
Thickness, mean lateral grain size (L_G), mean intergranular depth (ΔZ_{IG}) and roughness for the oxide layers formed on 316L stainless steel in simulated pressurized water reactor (PWR) environment at different oxidation time. Error margins were estimated by calculating confidence intervals with a 95% confidence level.

t_{ox}	Total thickness (inner + outer layer) (nm) [37]	L_G (nm)	ΔZ_{IG} (nm)	Roughness (RMS) (nm)
2 min (Tapping mode)	∼5 (2 + 3)	18.6 ± 1.9	3.9 ± 0.4	1.7
2 min (Contact mode)		29.1 ± 2.4	2.9 ± 0.4	2.1
10 min (Tapping mode)	∼12 (5 + 7)	32.8 ± 4.9	5.4 ± 0.6	4.2
10 min (Contact mode)		42.1 ± 3.3	3.8 ± 0.5	3.3
100 h (Tapping mode)	∼20 (11 + 9)	48 ± 4.9	6.7 ± 1.2	5.2