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Effect of water chemistry on the oxide film on Alloy 690 during simulated hot functional testing of a pressurised water reactor

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ABSTRACT

Electrochemical impedance spectroscopic measurements to follow the oxidation of Alloy 690 in high-temperature water environments simulating hot functional test (HFT) chemistries are presented and discussed. The thickness and in-depth composition of the formed oxides is estimated by X-ray photoelectron spectroscopy. Kinetic and transport parameters of the oxidation process are estimated by quantitative comparison of the results with the mixed-conduction model for oxide films. Based on the influence of LiOH and H_3BO_3 concentrations on the parameter values, conclusions for the relationship between HFT water chemistry and the electrical and electrochemical properties of the passive layer on reactor coolant circuit surfaces are drawn.

1. Introduction

Corrosion products released from component surfaces of a nuclear power plant primary loop can be carried with the coolant flow to the core, then deposit on the fuel elements and become activated. These activated corrosion products may again be released, transported by the coolant flow and subsequently deposited onto other component surfaces in the primary loop causing an increase in the local radiation levels, i.e. activity build-up. The source term of the process, the initial corrosion product release rate, is governed by the surface film properties of the components in question. The steam generator surface area is about 70% of the total surface area exposed to the coolant. Thus the corrosion product release from steam generator surfaces is dominating the extent of activity build-up in Pressurised Water Reactors (PWRs). In case of a new PWR plant the first passivation treatment during the Hot Functional Test (HFT) period is crucial in creating a surface film with as low as possible corrosion product release rate. During these tests that are carried out close to the operational temperature (above 280 °C), passivation of the reactor coolant system (RCS) takes place [1]. The tubing material selected for steam generators in modern PWRs is mainly Alloy 690. This has been the trend after Alloy 600 tubing was found to suffer from IGSCC in several plants.

For a range of PWRs the normal method for RCS passivation during HFT was to operate at 1–2 wppm of Li (added as LiOH) at $T > 260\,°\mathrm{C}$, with Cl^- and $F^- < 150$ wppb, dissolved $O_2 < 100$ wppb for 3–4 weeks [2]. As a next step, Garbett and Mantell [2] reported the use of a modified HFT water chemistry, the length of the passivation stage with ca. 1.5 wppm Li as LiOH being reduced to 10 days. This was followed by 11 days at beginning-of-cycle water chemistry (1150 wppm B and 1.8–2.0 wppm Li). Additionally, 30–40 $cm^3\,kg^{-1}$ of dissolved H_2 was present throughout HFT. Based on a long-term follow-up of the kinetics of corrosion release of both soluble species and particulate solids [3,4] it has been concluded that the primary circuit surfaces were well passivated during commissioning. Further, Yamada et al. [5] performed autoclave studies of the effect of HFT water chemistry (Li: 0.5 wppm, DH_2: 30 $cm^3\,kg^{-1}$, $DO_2 < 10$ wppb) on corrosion product release rate from alloys 600 and 690. After a 600 h test run under simulated HFT conditions, part of the specimens were exposed to simulated power operation conditions (500 ppm B as H_3BO_3, 1 wppm Li as LiOH, 30 $cm^3\,kg^{-1}$ of dissolved H_2 and <10 wppb of dissolved O_2 for additional 3000 h. Kadoya [6] reported results from using similar HFT chemistry at Ikata 3 with Alloy 690 steam generator tubing. Based on the data of Ni concentration in the coolant a clear radiation source reduction effect due to the improved HFT water chemistry was evaluated. In addition, Ito et al. [7] also found a considerable improvement in Fe and Ni release rates using similar HFT water chemistry at Genkai 4. At the moment, there is no consensus on the optimal concentration of LiOH to be used during HFT. In addition, the possible benefit from adding boric acid in the HFT passivation treatment is somewhat unclear.

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In recent years, a number of extensive studies of the corrosion and oxidation behaviour of Alloy 690 in high-temperature water have been carried out using mainly ex situ characterisation techniques [8–23]. The corrosion film was found to consist of a continuous and uniform Cr-rich internal layer and an external layer, the composition, morphology and microstructure of which depended on the test conditions and duration [8–11]. Experiments performed with gold markers and Rutherford Backscattering Spectroscopy revealed that the passive film formation involves anionic transport as the dominating process. This result was confirmed by experiments achieved with two sequences of corrosion in a $H_2{}^{16}O$ media and in a mixed $H_2{}^{16}O$–$H_2{}^{18}O$. The localisation of ^{18}O in the inner layer underlined an oxidation mechanism due to oxygen diffusion via short circuits (like grain boundaries) in the oxide [14]. Grain boundary diffusion coefficients in a chromite-like inner layer were estimated to be in the range 2×10^{-18}–1×10^{-17} cm^2 s^{-1} at 325 °C and successfully compared to values extrapolated from higher temperature. Very recently, the nature and the structure of the oxide on Alloy 690 in nominal primary PWR coolant at 325 °C have been investigated by TEM and SEM [16]. TEM observations revealed an oxide layer divided in two parts. The inner layer was found to be mainly composed of a continuous spinel layer, identified as a mixed iron and nickel chromite ($Ni_{1-x}Fe_xCr_2O_4$). Moreover, nodules of Cr_2O_3, with a size of about 5 nm, were present at the interface between this spinel and the alloy. No chromium depletion was observed in the alloy at the alloy/oxide interface, in contrast to previous studies [9,11]. The outer layer was composed of large crystallites corresponding to a spinel structure rich in iron ($Ni_{1-z}Fe_{2+z}O_4$) resulting from precipitation phenomena. In the outer layer, partially hydrated nickel hydroxide was also observed. On the other hand, electrochemical measurements of the behaviour of Alloy 690 in high-temperature water electrolytes are rather scarce [18,19,24,25]. Electrochemical impedance spectroscopic (EIS) data of Alloy 690 were reported at 320 °C in sulphate solutions only and qualitatively interpreted by the formation of a passive layer through which ionic transport was clearly detectable [25]. Attempts to correlate thermodynamic predictions, electrochemical measurements and surface analytical characterisations were made in alkaline sulphate solutions simulating abnormal SG crevice chemistry in the secondary circuit of PWRs [18,19]. Recently some of us attempted at interpreting simultaneously in situ EIS data for binary Ni–Cr alloys in borate buffer solution at 300 °C and XPS analyses of films formed on Alloy 600 in nominal PWR primary coolant [26] by the Mixed-Conduction Model (MCM) for oxide films on nickel-based alloys [27,28]. With the obtained set of parameters, steady-state current densities and impedance responses during oxide film growth on Ni–15%Cr and Ni–20%Cr alloys in 0.1 M $Na_2B_4O_7$ at 300 °C have been predicted in a broad potential range. In addition, a self-consistent set of parameter values has been found to reproduce successfully the film thickness vs. time relationship on Alloy 600 in simulated PWR water up to several thousands of hours. This result supports the view that the oxidation of nickel-based alloys in high-temperature water is controlled by generation, solid-state transport and consumption of point defects in the inner layer of oxide.

The main goal of the present paper is to indicate which HFT procedure produces an oxide film with optimal electrical, electrochemical and transport properties, based on a quantitative interpretation of in situ EIS and ex situ XPS data for Alloy 690 in simulated PWR HFT water chemistry. For the purpose, impedance spectra for Alloy 690 in electrolytes containing 0.5–2 ppm of Li with or without 245–1200 ppm of B were measured for times up to 100 h at 292 °C in both an autoclave and a flow-through cell connected to a recirculation loop to simulate HFT water chemistry. The obtained oxide films were characterised by XPS to estimate the in-depth distribution of chemical states of main layer constituents. The relevant kinetic and transport parameters of the oxidation process are estimated by a simultaneous interpretation of the in situ EIS and ex situ XPS data, as already described for films on AISI 316 in nominal and high-pH PWR water [29]. An adaptation of the MCM to the specific system under study is quantitatively compared to the EIS data, whereas the XPS depth profiles are interpreted by a model describing the transport of individual constituents of the oxide that has been developed earlier by some of us [30]. Finally, conclusions on the effect of Li and B concentration on the electrochemical and transport properties of the oxide in view of the role of HFT in the stable and prolonged PWR operation are drawn.

2. Experimental

2.1. Materials and conditions

Working electrodes were manufactured from Alloy 690 tubes (UNS N06690, courtesy of EPRI NDE Centre, nominal composition in wt.%: Cr 30.3, Fe 9.4, Si 0.3, Mn 0.3, Cu 0.04, C 0.02, P 0.011, S 0.0002, balance Ni), the material being in an annealed condition, and were used as-received to preserve the original microstructure. The measurement Ni-wires with a diameter of 0.8 mm were mechanically attached to the specimens and the connection was covered with multilayered PTFE tape. An internal Pd reference electrode polarised with a negative current of 5 μA cm^{-2} to approximate the reversible hydrogen electrode (RHE), i.e. the H_2/H^+ equilibrium potential in the respective solutions, was used. The potentials were converted to the SHE scale by the Nernst equation after calculating the solution pH at the temperature. A cylinder made of Pd and placed around the specimen was employed as a counter electrode. The measurements were performed at 292 ± 1 °C in a stainless steel autoclave connected to a recirculation loop that enabled the refreshing of the electrolyte in the autoclave ca. twice per hour. Some experiments were carried out in a flow-through cell to check the effect of hydrodynamics (flow rate 0.4 cm s^{-1}, i.e. about 20 times higher than in the autoclave). The electrolytes (0.25–1.0 mmol l^{-1} LiOH, 0–0.63 mmol l^{-1} H_3BO_3) were prepared from analytically pure chemicals and deionised water. A hydrogen overpressure of 1.5 bar was maintained in the feed water tank ensuring a concentration of 30 cm^3 (STP) kg^{-1} (1.3 mmol l^{-1}) of dissolved H_2 in the autoclave or the flow-through cell, respectively.

2.2. Apparatus and procedure

Impedance spectra were obtained with a Solartron 1287/1260 system controlled by Zplot/Zview software in a frequency range of 80 kHz to 0.5 mHz at an ac signal amplitude of 10 mV (rms) roughly at every three hours till the end of exposure at open circuit. Validation of the impedance spectra was performed by checking the linearity condition, i.e. measuring spectra at different signal amplitudes. The spectra were also found to be compatible with the Kramers–Kronig transforms within the experimental error (±2% by magnitude and ±3° by phase angle). Points that did not comply with the transforms (usually at both ends of the measured frequency range) were rejected. For the simulation and fitting of impedance spectra to the transfer function derived from the kinetic model, a Microcal Origin-based software routine was employed. XPS spectra were registered using an ESCALAB Mk II (VG Scientific) electron spectrometer with a base pressure of ≈10^{-7} Pa. The photoelectrons were excited with a Mg Kα (1253.6 eV) X-ray source and the analyzer pass energy was 20 eV. The B1s, C1s, Li1s, O1s, Fe2p, Cr2p, and Ni2p photoelectron lines were recorded and the binding energies were calibrated versus the C1s peak. To obtain depth profiles, Ar ion milling was used and the conversion of the sputtering time