

In situ Synchrotron X-ray Investigation of Alloy Corrosion in Supercritical Water

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The supercritical water cooled reactor (SCWR) is one of the most promising advanced nuclear reactor designs, with a superior projected thermal efficiency compared to the currently operating light water reactors. A key barrier to the economic viability of the SCWR for electricity generation is the prevailing corrosion of the structural alloy materials in the reactor core due to the presence of supercritical water (SCW) at high temperature (up to 550°C) and pressure (25MPa). A fundamental understanding of the oxidation and corrosion mechanisms of alloys in SCW environments is needed for achieving revolutionary advances in the durability of alloys in SCW.

In order to investigate the initial oxidation behavior of alloys in SCW, we conducted experiments using interface-sensitive x-ray techniques at the Advanced Photon Source. These experiments have been the first ever *in situ* synchrotron x-ray investigation of alloy surfaces under the extreme conditions of high pressure high temperature water up to the supercritical water conditions. We used a microreactor cell¹ provided by Arizona State University (ASU) capable of achieving high temperature and pressure experiment conditions and allowing x-rays to penetrate through its windows. The cell was mounted on a diffractometer for x-ray reflectivity and x-ray diffraction measurements (Fig. 1). The pressure inside the cell was controlled using a pressure regulator on a 6000psi-He cylinder. A brass heater that was specifically designed to house the cell was used to electrically heat the cell. The cell used two moissanite windows of 2 mm in thickness. These windows limited us to high-energy x-rays of 25keV for our initial measurements and achieved 10% transmission.

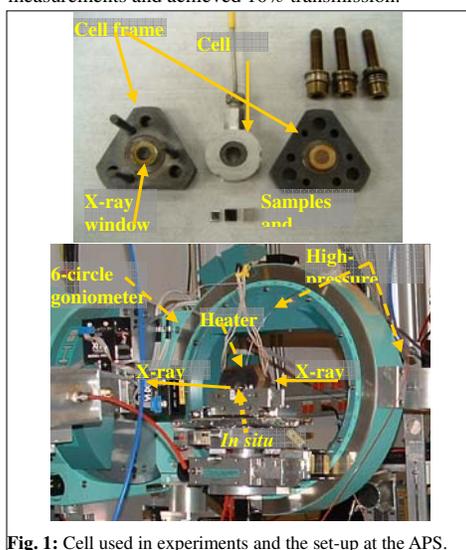


Fig. 1: Cell used in experiments and the set-up at the APS.

The alloys were supported inside the cell, which was subsequently filled with water and pressurized up to 15MPa for Ni 200 and 25 MPa for SS304. The system was then slowly heated to subcritical (320°C) and supercritical (400°C) water temperatures.

We demonstrated for the first time under the stable supercritical water conditions: (i) The ability to perform *in situ* synchrotron x-ray scattering from alloy-SCW interfaces to measure changes in surface roughness, formation of adsorbed layers, and formation of oxide phases; (ii) the capability for *in situ* depth-sensitive powder diffraction measurements by means of changing the incident angle of the x-ray beam on the surface of the alloy in the cell. Using these capabilities, we were able to follow the initial adsorbed layers and the oxide growth in SCW on two different materials. We identified continuous, conformal oxide formation on both a Ni 200 alloy and stainless steel 304 (SS304). We demonstrated that the x-ray incidence angle can be varied to increase the sensitivity of the measurement to the top layers of the sample, allowing us to do depth profiling of oxide layers under *in situ* conditions of supercritical water.

The first oxide layer observed on the 304SS when the sample was heated to 380°C (Fig. 2, the green curve) was Cr₂O₃. Taken together with the reflectivity data, this suggested that a thin amorphous film first formed on the surface which then grew and became crystalline Cr₂O₃ at higher temperatures over several hours of our measurements. Chrome oxides are known to form protective films on austenite stainless steels in oxidizing conditions. Our observation that Cr₂O₃ starts to form at subcritical water conditions fits well with other studies² showing that at constant pressure, water becomes most corrosive just below the supercritical temperature³. This finding is in contrast to *ex situ* studies of 304SS that report FeCr₂O₄ spinel for boiling water reactor conditions at 288°C⁴. This observation suggests the value of *in situ* studies to probe the oxidation from its early to late stages without being compromised by removing the sample from the corrosion environment, for a wide range of materials that function in high-temperature, high-pressure water.

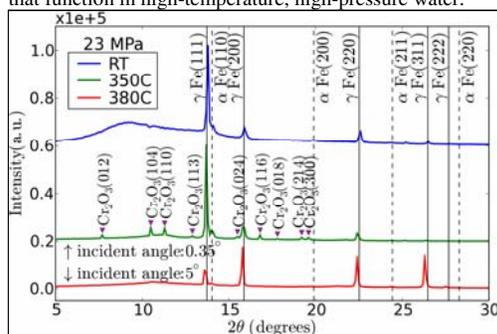


Fig. 2: X-ray powder diffraction of the SS304 alloy under high pressure at increasing temperature

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