

## Effects of pH on S-induced passivity degradation of Alloy 800 in simulated crevice chemistries

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Alloy 800, as one of the key materials in steam generator (SG) tubes, is widely used in CANDU power plant.

The degradation mechanism of passive film is a topic of great interest in theoretical studies and in industrial operations such as nuclear plant. Sulfate impurities and released resins accumulate in the crevice between tubing and support plate. N<sub>2</sub>H<sub>4</sub> can react with these species to produce lower-valence sulfur according to thermodynamic inclination of such reactions to occur. Sulfur of lower-valences (+2.5, +2 or -2) tend to facilitate the entry of hydrogen into metals and to accelerate general and localized corrosion of Alloys 600 and 690[1-3]. Therefore, low-valence sulfur-induced passivation degradation is one of the major problems for steam generator (SG) tubing materials.

Generally, alloy degradation induced by low-valence sulfur has been extensively studied in the areas such as fossil fuel, petroleum industry, paper machines, microbial corrosion and nuclear power systems[4, 5]. However, the effects of lower-valence sulfur on passivity degradation have not been studied systematically over the relevant range of pH. The interactions among various species may have profound impacts on passivity and SCC susceptibility of materials. These interactions are often very complex and may heavily depend on the test conditions. One of the examples is the effects of sulfur contamination on the SCC behavior, which has been found to be strongly dependent on the solution pH [6].

The anodic films degradation caused by sulfur impurity could be resulted from the changes in the film structures. The composition and structure of a passive film on a Ni–Cr–Fe alloy are dictated by the environment where the passive film forms. Unfortunately, very limited experimental data are currently available to reveal the interactive effects of important dissolved species that are commonly found in the crevice chemistry. The comprehensive understanding of the synergistic effects among these species on the corrosion behavior of SG tubing alloys is practically important for optimizing the water management strategy to extend the service life of nuclear power generation systems.

In this work, the effects of pH on S-induced passivity degradation of Alloy 800 in simulated crevice chemistries at 25 °C with and without sulfur contamination are evaluated using electrochemical noise (EN), electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), secondary ion mass spectroscopy (SIMS), and Mott-Schottky analysis.

The results showed that in neutral crevice chemistry, reduced S lowered the breakdown potential of Alloy 800

by 100-600 mV in the solution with chloride ions, depending on the concentration and the valence of the sulfur species. Mott-Schottky analyses showed that the passive films formed in chloride-containing solutions without and with reduced sulfur solution exhibited n-type semiconductor, possibly due to the predominance of oxygen vacancies as the crystallographic defects. Due to the catalytic effect of thiosulfate on the transfer of Me<sup>Z+</sup> from the oxide to the electrolyte, it inhibited the healing process of repassivation once the film broke down. Thiosulfate could be easily reduced to adsorbed sulfur or sulfide, especially on the active sites where passive film breakdown was induced by Cl<sup>-</sup>.

In basic crevice chemistry, OH<sup>-</sup> decreased the detrimental effect of reduced sulfur, leading to a wide potential range of passivation. The passive film in basic crevice chemistry behaved as p-type and cation vacancies were considered as majority defects.

In acid crevice chemistry, Alloy 800 suffered uniform corrosion, and active-passive transformation was seen in S-free solution. The addition of reduced sulfur changed the active-passive transformation to active anodic dissolution.

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