Passivity breakdown of Ni-Cr-Fe alloys in chloride plus thiosulfate solutions at the open circuit potential

Abraham A. BECERRA ARANEDA[1], Mariano A. KAPPES[1], Martín A. RODRÍGUEZ[1], Ricardo M. CARRANZA[1]

[1] National Commission of Atomic Energy of Argentina, Argentina

Thiosulfate, in the presence of chloride excess, can promote pitting corrosion of Ni-Cr-Fe alloys, such as UNS N06600 (alloy 600), N06690 (alloy 690) and N08800 (alloy 800). Currently, these alloys are used in steam generator (SG) tubing of nuclear reactors. Alloys 690 and 800 exhibit two potential-dependent submodes of pitting corrosion in chloride solutions with little thiosulfate additions: low potential pitting corrosion (LPPC), close to the open circuit or corrosion potential (E_{CORR}), where both thiosulfate and chloride act synergically; and high potential pitting corrosion (HPPC) of similar characteristics to conventional chloride pitting. Alloy 600 only evidence LPPC in solutions where alloys 690 and 800 show both LPPC and HPPC. The threshold amount of thiosulfate required for LPPC occurrence decreases in the order: alloy 600 > alloy 800 > alloy 690. The above mentioned submode of pitting is relevant since those conditions can be produced in SG under wet lay-up.

To gain insight about the LPPC mechanism, in this work we studied the passive film properties at E_{CORR} of alloys 600, 690 and 800 in chloride plus thiosulfate solutions. The alloys were tested in solution annealed condition. Deaerated 1 M NaCl with $5x10^{-5}$ to 10^{-3} M $Na_2S_2O_3$ additions at room temperature were used as testing solutions. E_{CORR} was recorded for periods of 1, 10, 20, 30, 40 and 50 h. Electrochemical impedance spectroscopy (EIS) measurements were performed. Eventual corrosion damage was characterized by optical microscopy and scanning electron microscopy after electrochemical tests.

The corrosion protection of passive film increased in the order: alloy 690 > alloy 800 > alloy 600, which was related to the chromium contents of the alloys. EIS results indicated a more protective passive film on tested alloys as the exposure time at E_{CORR} increased, in 1 M NaCl solutions.

When thiosulfate was added to 1 M NaCl solutions, LPPC was observed at E_{CORR} in alloys 600 and 800 for thiosulfate additions between $5x10^{-5}$ and $5x10^{-4}$ M. LPPC did not occur on alloy 690 at E_{CORR} in the chloride plus thiosulfate solutions studied. In alloy 800, the least protective passive film was observed in solutions with 10^{-4} M thiosulfate; while in alloy 600, the least protective film was observed for $5x10^{-5}$ M thiosulfate. Hemispherical pits with black sulfur-rich corrosion deposits characterized the attack by LPPC.