Stress corrosion cracking and surface oxidation behavior of Ni-base alloys exposed to simulated PWR primary water

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Primary water stress corrosion cracking (PWSCC) of Ni-base Alloy 600 (Ni-16Cr-8Fe in wt%) has been a major concern in the primary sides of pressurized water reactors (PWRs). In response to the cracking problems of Alloy 600, another solid-solution strengthened Ni-base Alloy 690 (Ni30Cr10Fe in wt%) has become the common replacement material for use in PWR service. Alloys 600 and 690 have an identical crystal structure and similar mechanical properties; however, there are noticeable differences in the corrosion resistance and cracking behavior between them owing to their different Cr contents. The aim of the present study is to investigate the resistance of Alloys 600 and 690 to PWSCC, and to reveal the different characteristics of PWSCC in terms of cracking and internal oxidation behavior.

PWSCC testing of Alloy 600 and Alloy 690 was conducted using 1/2T compact tension (CT) specimens at 325 . The test conditions were 1200 ppm B (weight) as H_3BO_3 and 2 ppm Li (weight) as LiOH in pure water, a dissolved oxygen content below 5 ppb, a hydrogen content of 30 cm^3/kg H_2O, and an internal pressure of 15.9 MPa. The crack growth rates (CGRs) were measured depending on the stress intensity factor at a crack tip. A surface oxidation test using plate specimens was conducted in the same test conditions as those of the CGR test for a period of 3600 hours. After the tests, cracking properties and surface oxidation layers were precisely characterized using SEM, high-resolution TEM, STEM/EDS, and STEM/EELS.

The average CGR of Alloy 600 was measured as 1.5×10^{-8} mm/s when the stress intensity factor at a crack tip was maintained at 40 $MPa{\cdot}m^{1/2}$, whereas no evidence of Alloy 690 cracking was found under the present conditions. This means that the resistance to PWSCC of Alloy 690 is much higher than that of Alloy 600. From a microscopic examination on crack propagation, it was found that the predominant failure mode of Alloy 600 was intergranular (IG) SCC, which indicates that the grain boundaries are preferential paths for cracking. It was revealed from a microscopic investigation on the surface that oxygen diffused into the grain boundaries of Alloy 600 from the external primary water, resulting in IG oxidation. The most important finding in Alloy 690 was that the internal oxidation into the bulk grains was promoted resulting in the formation of relatively thick internal oxidation layer, whereas the IG oxidation was significantly suppressed owing to the continuous innermost Cr_2O_3 layer which formed around a grain boundary. The innermost Cr_2O_3 layer was formed through inward diffusion of oxygen from the surface and outward diffusion of Cr, resulting in Cr depletion along the grain boundary. From the present results, it is believed that the different IG oxidation behavior of Alloys 600 and 690 appear to lead to the different cracking resistance capabilities and cracking behaviors in these alloys.