# Crevice Corrosion Characteristics of Alloy 690 in High-Temperature Oxygenated Pure Water

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<u>Abstract</u>: An exposure testing device for crevice corrosion simulation in high-temperature pressurized water was used to investigate the crevice corrosion characteristics and related mechanisms of Alloy 690 in high-temperature oxygenated pure water. The morphologies, phase structure and compositions of oxide films along the crevice wall were investigated using stereomicroscope, SEM-EDS, XRD, Raman spectroscopy and XPS. It was found that different hydrochemistry conditions and potential drop affected the development of oxide films on Alloy 690 within the crevice. The thick oxide film formed at crevice mouth mainly consisted of compact NiO and NiFe<sub>2</sub>O<sub>4</sub> due to the precipitation of Ni<sup>2+</sup> and Fe<sup>2+</sup>, while the thin oxide film formed within the crevice mainly consisted of an outer layer of Cr(OH)<sub>3</sub> and (Fe, Ni)Cr<sub>2</sub>O<sub>4</sub>, and a continuous inner layer of Cr<sub>2</sub>O<sub>3</sub>, which was due to the hydrolysis of Cr<sup>3+</sup> and decreased of pH value of the crevice solution. Possible mechanisms of oxide films formed at different sites along the crevice in high-temperature water are discussed.

Keywords: crevice corrosion, Alloy 690, high-temperature water, oxide film, water chemistry

#### **Introduction**

Crevice corrosion is an undesirable degradation of the structural materials in pressurized water reactor (PWR) nuclear power plants (NPPs). Many key parts of steam generators in PWR NPPs are easily attacked by the crevice corrosion during long-term service due to the presence of geometric crevices during long-term service in high-temperature pressurized water, such as the tube/tube sheet, the tube/support plate and the deposits/tube crevices [1-4], which is one of potential threats to the safety of PWR NPPs. The presence of geometric crevices may result in a restrict ion of the mass transport between the crevice and bulk solutions. As a result, the ionic concentrations within the crevice become much higher than those in the bulk solution, which makes the solution within the crevice become more aggressive and then damages the passive film. Since the crevice corrosion often takes place in occluded regions and has a long incubation period, it is rather difficult to be on-line detected or monitored. However, once it is initiated it could accelerate the damage of materials within crevice rapidly. The behaviour and mechanism of crevice corrosion have been investigated in lots of previous work and two mechanisms have been proposed to explain the crevice corrosion, including critical crevice solution and potential drop theories [5, 6]. Both of theories have the same viewpoint that oxygen is depleted within the crevice. The dissolved oxygen (DO) concentration within the crevice solution is thus one of the most important factors affecting the crevice corrosion behaviour. In the present work, an exposure test device for crevice corrosion simulation in high-temperature pressurized water has been used to investigate the crevice corrosion behaviour and related mechanism of Alloy 690 in hightemperature oxygenated pure water. Morphologies, phase structure and compositions of oxide films along the crevice wall have been carefully investigated and possilbe corrosion mechanisms are also discussed.

# **Experimental**

The simulating test device of crevice corrosion in high-temperature pressurized water was composed of zirconia bolt, two samples of Alloy 690 and one nut with the same material, which can withstand high-temperature water. The sizes of the bottom and top parts were different in order to adjust the crevice length. The bottom was immovable and the width of crevice was adjusted accurately through the rotating angle of the top part. Exposure tests of the crevice specimens in high temperature pressurized water were performed in a refreshed autoclave made of 316 SS with a volume of 2 L. More detailed information of the crevice device and testing system has been described in the previous work[7, 8].

The composition of Alloy 690 used in the present work (wt.%) is 0.03%C, 0.013%N, 29.73%Cr, 10.5%Fe, 0.29%Si, 0.29%Mn, 0.2%Ti, 0.2%Al, 0.01%Cu, 0.001%S, 0.007%P, and Ni balance. The specimens were mechanically abraded using silicon-carbide paper up to 2000 grit and degreased with ethanol in ultrasonic washer before the exposure tests. The expsoure test solution is refreshed deionized water. The inlet water conductivity is 60-75 nS/cm. The flow rate is 9-10 L/h and the pressure is 8 MPa. The test temperature in autoclave is controlled as  $290 \pm 2^{\circ}$ C and the DO of 3 ppm (by weight) and 5 ppb are adopted to investigate the effect of DO concentration on crevice corrosion behavior.

After exposure tests, the surfaces of specimens were cleaned using cotton that absorbed deionized water and dried carefully using absorbent paper. The surface macro-morphologies of specimens were examined using a Leica S6D and an OLS4000 3D stereomicroscope. The micro-morphologies of the specimens were examined using a scanning electron microscopy (SEM) (FEI XL30) equipped with an energy-dispersive spectrometer (EDS). The structure of oxide film was analyzed by a BWS905 custom Raman system and a D/Max 2400 X-ray diffraction (XRD) analyzer with Co K alpha radiation. An ESCALAB250 X-ray photoelectron spectrometer (XPS) was used to analyze the thickness and composition of oxide film. More detailed information of depth profiling by XPS has been described in the previous work [9].

# **Results and Discussion**

Fig. 1 shows the surface macro-morphologies of Alloy 690 crevice corrosion specimens after 200 h and 500 h exposure tests in 290°C water containing 3 ppm DO. Different colors and corrosion morphologies were observed on the free and crevice surfaces, suggesting that crevice corrosion surely took place during the exposure tests in oxygenated high-temperature water and the oxide films were different at different sites along the crevice. The surface of specimens can be divided into four regions, namely, free surface (region A), crevice mouth (region B), within the crevice (region C) and deeper site within the crevice (region D) (Fig. 2c and 2d). The width of region B for the 500 h exposed specimen was much wider than that for the 200 h exposed one, indicating that the crevice corrosion became serious with increasing the exposure time.

Fig. 2 show the SEM morphologies and EDS results of oxide films on the free and crevice surfaces of Alloy 690 crevice corrosion specimens after 500 h exposure tests in 290°C water containing 3 ppm DO. A kind of sparse oxide clusters with some straight sidesteps were observed in the region A. The inner layer of oxide films appeared porous (Fig. 2a). The previous work has proven that the oxide clusters were spinel oxides and the porous inner oxides were NiO [9, 10]. A few oxide clusters, numerous small oxide particles and minor plate-like oxides were observed in the region B (Fig. 2b). EDS results indicated that the Fe

and Ni contents in the oxide clusters and small oxide particles in the region B were different. Some spinel oxides, needle-like oxides and lamellar oxides were observed in the region C (Fig. 2c). Some large lamellar oxides were observed in the outer layer and small oxides were found in the inner layer (Fig. 2d).



Fig. 1 Surface macro-morphologies of Alloy 690 crevice corrosion specimens after 200 h and 500 h exposure tests in 290°C water containing 3 ppm DO.



Fig. 2 SEM morphologies and EDS results of oxide films on the free and crevice surfaces of Alloy 690 crevice corrosion specimens after 500 h exposure tests. (a) region A (b) region B (c) region C (d) region D.

Fig. 3 shows the XRD patterns (left) and Raman spectroscopies (right) of the oxide films on the free and crevice surfaces of Alloy 690 after 500 h exposure test in 290°C water containing

3 ppm DO. The characteristic peaks of spinel oxides and NiO were detected in the regions A, B and C. The weak characteristic peak of  $Ni(OH)_2$  was found only on the free surface. The peak intensity of spinel oxides on the free surface was stronger than that on the crevice surface. The Raman characteristic peaks (560 cm<sup>-1</sup> and 693 cm<sup>-1</sup>) of spinel oxides [11-14] were detected in all regions. The Raman characteristic peaks (480 cm<sup>-1</sup>) of NiO [12, 13, 15] were detected in the regions A and B. It was found that the spinel oxides at the outermost surface in the region B were more than those in the other regions, and the region D had least spinel oxides.



Fig. 3 XRD patterns (left) and Raman spectroscopies (right) of the oxide films on the free and crevice surfaces of Alloy 690 after 500 h exposure test.

Detailed XPS spectra of Cr 2p3/2, Fe 2p3/2, Ni 2p3/2, O1s in the oxide films from the free surface to the deeper site within the crevice of Alloy 690 after 500 h exposure test were analyzed carefully. At the free surface (region A), the Ni 2p3/2 spectrum consisted of NiO, NiFe<sub>2</sub>O<sub>4</sub>, NiO and Ni(OH)<sub>2</sub> (Fig. 4). The Fe 2p3/2 spectrum consisted of Fe<sup>3+</sup> and a small amount of  $Fe^{2+}$ . The O 1s spectrum shows that the hydroxides content was higher than oxides. It is concluded that the oxide films mainly consisted of NiO, (Ni, Fe)Fe<sub>2</sub>O<sub>4</sub> and a small amount of Ni(OH)<sub>2</sub> by combining the XPS results with SEM, XRD and Raman results, which is consistent with the work of Kuang [9, 10]. At the crevice mouth (region B), the Ni 2p3/2 spectrum consisted of NiO, NiFe<sub>2</sub>O<sub>4</sub>, Ni<sup>0</sup> and a small amount of Ni(OH)<sub>2</sub> after 45 s sputtering. According to the SEM-EDS results, the presence of NiFe<sub>2</sub>O<sub>4</sub> and NiO in oxides was confirmed. The OH peak was detected in the oxides, and the very low Fe and Cr contents in the oxides proved that the Ni(OH)<sub>2</sub> was present. It was reported that the plate-like oxide formed on Ni-based alloy was Ni(OH)<sub>2</sub> (Fig. 2b) [9]. Within the crevice (region C), the Cr 2p3/2 spectrum exhibited only  $Cr^{3+}$  peak and its satellite peak (Fig. 5). The Ni 2p3/2 spectrum consisted of NiO, NiCr<sub>2</sub>O<sub>4</sub>, Ni<sup>0</sup> and Ni(OH)<sub>2</sub>, and the change of intensity of Ni<sup>0</sup> peak was consistent with that at the crevice mouth. The XRD and Raman results indicated that there were spinel oxides in the oxide films. It is believed that the spinel oxide corresponded to NiCr<sub>2</sub>O<sub>4</sub>. The presences of Cr(OH)<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> could be verified by combining the Cr 2p3/2, Ni 2p3/2 and the O 1s spectrums. The XPS and Raman results indicated that the oxide film in the region D mainly contained a large amount of Cr(OH)<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and a small amount of FeCr<sub>2</sub>O<sub>4</sub>. From the outer to inner layer of oxide film, the  $Cr(OH)_3$  content in the oxide film gradually decreased, while the Cr<sub>2</sub>O<sub>3</sub> content increased.

The present SEM observation and the analyses of XRD patterns, Raman spectra and XPS in the present work indicate that the oxide films on the free and crevice surfaces of Alloy 690 after exposure tests in 290°C pure water containing 3 ppm DO have different compositions and structures, suggesting that crevice corrosion surely occurs during the exposure tests and

the oxidation mechanisms at different sites of crevice specimen are different in high-temperature pure water. The oxide films on the free surface had similar composition and



Fig. 4 Detailed XPS spectra of Cr 2p3/2, Ni 2p3/2, O1s in the oxide film formed at the crevice mouth of Alloy 690 after 500 h exposure tests in 290 °C water containing 3 ppm DO.



Fig. 5 Detailed XPS spectra of Cr 2p3/2, Ni 2p3/2, O1s in the oxide film formed within the crevice of Alloy 690 after 500 h exposure tests in 290 °C water containing 3 ppm DO.

structure as the general corrosion. The outer layer of oxide film was mainly Ni-Fe spinels and the inner layer was porous NiO (Fig. 2a). However, the hydrochemistry conditions (including metallic ions, DO and pH) within the crevice change with increasing the exposure time, resulting in that different types of oxides forms in different regions. The presence of the crevice geometry significantly affects the mass transport between the bulk and crevice solutions, resulting in ionic concentration gradients and depleted of oxygen within the crevice [5, 16]. Since the consumption rate of DO within the crevice is faster than the diffusion rate of DO from the bulk solution into crevice solution, the DO plays a key role in the oxidation process of crevice corrosion. The crevcie depth in the present work was 4 mm, which can lead to a rapid decrease of DO concentration within the crevice. Decreasing DO concentration could result in a lower electrochemical corrosion potential (ECP) of the metal [17]. Therefore, the presence of DO concentration gradient from the crevice mouth to the deeper site within the crevice can result in an obvious potential drop within the crevice. In addition, the metallic ions produced by dissolution within the crevice are enriched due to the restricted geometry. The hydrolysis of these metallic ions can result in a decrease of pH value in the solution within the crevice. As a result, the growth mechanism of oxides within the crevice is different from that on the free surface.

According to the Pourbaix diagrams for Ni-Cr-Fe alloy in 300°C pure water [18, 19], the stable oxides become NiFe<sub>2</sub>O<sub>4</sub>, NiO, NiCr<sub>2</sub>O<sub>4</sub>, FeCr<sub>2</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> with decreasing the potential value. Kim and Andresen [17] reported that the ECP of Alloy 182 was around 0.2  $V_{SHE}$  in 288°C pure water containing 2 ppm oxygen. In the present work, the ECP of Alloy 690 should be more than 0.2  $V_{SHE}$  in 290°C pure water containing 3 ppm oxygen and the pH of 290°C pure water is around 5.6. It can be found from the Pourbaix diagrams that the NiFe<sub>2</sub>O<sub>4</sub> is stable on the free surface. The ECP of Alloy 690 at the crevice mouth is lower than that at free surface. The formations of NiFe<sub>2</sub>O<sub>4</sub> on the free surface and NiO at the crevice mouth are consistent with ECP distribution.

Within the crevice (regions C and D), with the development of crevice corrosion, the solution tends to become acidic due to metallic ion hydrolysis. The hydrolysis constant of  $Cr^{3+}$  is higher than that of Fe<sup>2+</sup> and Ni<sup>2+</sup>, resulting in formation of large amount of Cr(OH)<sub>3</sub> in the outer layer of oxide films according to reactions (1) and (2) [16, 20].

	<u> </u>
$Cr^{3+}+3H_2O \rightarrow Cr(OH)_{3(aq)}+3H^+$	(1)
$Cr(OH)_{3(aq)} \rightarrow Cr(OH)_{3(s)}$	(2)

In the present work, XPS results suggest that the content of  $Cr(OH)_3$  gradually increases with increasing the crevice depth, which prove that the  $Cr^{3+}$  hydrolysis becomes increasingly serious, resulting in more severe acidification of the crevice solution. White et al. [16] found that  $Cr(OH)_3$  could be stable in an acidic solution with a pH greater than 2.5. According to the Pourbaix diagram [19], FeCr<sub>2</sub>O<sub>4</sub> and NiCr<sub>2</sub>O<sub>4</sub> are stable in high-temperature water when the pH value is greater than 3.5 and 4.8, respectively. Therefore, the  $Cr(OH)_3$  and Cr-rich spinel oxides within the crevice are stable in the present work.

In the region within the crevice near the crevice mouth (region C), the DO concentration is not zero and there are a higher  $Ni^{2+}$  content and a lower  $Fe^{2+}$  content, resulting in the formation of Ni oxides and hydroxides. The additional  $Ni^{2+}$  may be oxidized to  $Ni(OH)_2$  and NiO. The Cr(OH)<sub>3</sub> still exists at the outmost layer of oxide film due to the hydrolysis of Cr<sup>3+</sup>. Thus from the outer to inner layer of oxide film, the content of metal hydroxides gradually decreases, while the content of metal oxides gradually increases.

At the deeper site within the crevice (region D), with the development of crevice corrosion, the DO concentration is close to zero, indicating that the ECP of Alloy 690 is around -0.5  $V_{SHE}$  [21]. The pH of the solution is close to 5 [22]. According to the Pourbaix diagrams [18, 19], the FeCr<sub>2</sub>O<sub>4</sub> spinels and Cr<sub>2</sub>O<sub>3</sub> are stable under the condition of acidity and low potential. As Fe<sup>2+</sup> and Ni<sup>2+</sup> gradually diffuse outwards, some of Fe<sup>2+</sup> reacts with Cr oxides or hydroxides to form FeCr<sub>2</sub>O<sub>4</sub>. The small amount of Fe-Cr spinels formed initially may develop gradually through precipitation mechanism in the region D. Large amount of Cr(OH)<sub>3</sub> produced by ions hydrolysis react with the Cr from the matrix to produce Cr<sub>2</sub>O<sub>3</sub> at the metal/oxide film interface according to the reaction (3) [23].

 $Cr(OH)_3+Cr \rightarrow Cr_2O_3+3H^++3e^-$  (3)

Meanwhile, the  $Cr_2O_3$  also develops in the inner layer through inward diffusion of oxidant. As a result, from the outer to inner layer of oxide film, the  $Cr(OH)_3$  content in the oxide film gradually decreases, while the  $Cr_2O_3$  content increases.



Fig. 6 Schematic of crevice corrosion process of Alloy 690 in 290°C oxygenated pure water.

Fig. 6 shows the schematic of crevice corrosion process of Alloy 690 in 290°C oxygenated pure water. At the early stage, Fe and Ni selectively dissolve from the matrix into hightemperature water and the residual metallic elements are oxidized to Cr-rich oxides (Fig. 6a). With increasing exposure time, large (Ni, Fe)Fe<sub>2</sub>O<sub>4</sub> oxide particles in the outer layer and porous NiO in the inner layer form on the free surface due to the release of Cr into the solution as HCrO<sub>4</sub><sup>-</sup> under high-DO condition. The DO concentration in the crevice solution gradually reduces and the Fe<sup>2+</sup> and Ni<sup>2+</sup> are enriched at the crevice mouth. The DO concentration at the crevice mouth is much higher than that at the deeper site within the crevice. The NiFe<sub>2</sub>O<sub>4</sub> spinels gradually develop at the crevice mouth through the precipitation of the Fe<sup>2+</sup> and Ni<sup>2+</sup>, and the additional Ni<sup>2+</sup> ions react with DO to form NiO particles. Within the crevice, the hydrolysis of Cr<sup>3+</sup> produce large amount of Cr(OH)<sub>3</sub> and result in a decrease of pH value. The NiO and Ni(OH)<sub>2</sub> form due to large amount of Ni<sup>2+</sup> (Fig. 6b). With the development of crevice corrosion, more and more NiFe<sub>2</sub>O<sub>4</sub> and NiO form at the crevice mouth. These oxides enhance the occluded effect and lead to a more serious potential drop within the crevice. The pH value of crevice solution continually decrease and produce more  $Cr(OH)_3$  within the crevice. The low potential and the massive Ni<sup>2+</sup> lead to the formation of NiCr<sub>2</sub>O<sub>4</sub> within the crevice near the crevice mouth. At the deeper sites within the crevice, both the pH value and DO concentration are very low, resulting in formation of FeCr<sub>2</sub>O<sub>4</sub> spinel. At the same time, more and more Cr<sub>2</sub>O<sub>3</sub> form in the inner layer of oxide film. As a result, Cr(OH)<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and FeCr<sub>2</sub>O<sub>4</sub> spinels form at the deeper site within the crevice (Fig. 6c).

### **Summary**

The morphologies, structures and compositions of oxide films formed on Alloy 690 during crevice corrosion in 290°C pure water containing 3 ppm DO were investigated. The oxide film at crevice mouth mainly consists of compact NiO and NiFe<sub>2</sub>O<sub>4</sub>, while it consists of NiCr<sub>2</sub>O<sub>4</sub>, NiO, Cr<sub>2</sub>O<sub>3</sub>, Ni(OH)<sub>2</sub> and Cr(OH)<sub>3</sub> at the site near the crevice mouth within the crevice. The oxide film at deeper site within the crevice consists of an outer layer of Cr(OH)<sub>3</sub> and FeCr<sub>2</sub>O<sub>4</sub>, and a continuous inner layer of Cr<sub>2</sub>O<sub>3</sub>. The formation of Cr(OH)<sub>3</sub> results from the Cr<sup>3+</sup> hydrolysis within the crevice. With increasing the crevice depth, the Cr<sup>3+</sup> hydrolysis becomes increasingly serious, and thus the content of Cr(OH)<sub>3</sub> in oxide films gradually increases. The thin oxide film within the crevice is due to the formation of a protective inner layer of Cr<sub>2</sub>O<sub>3</sub>, while the thick oxide film at the crevice mouth is due to the precipitation of Ni<sup>2+</sup> and Fe<sup>2+</sup>.

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