Short-term Oxidation Behavior of Forged 316LN Stainless Steel in High-temperature High-pressure Water Postprint

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Abstract

Electron Backscatter Diffraction (EBSD) was employed to investigate the effects of forging and post-forging solution treatment on the grain size, residual strain, and grain orientation distribution of nuclear-grade 316LN austenitic stainless steel (316LNss), and to analyze the morphology and composition of surface oxide films formed on as-received (i.e., unforged) and forged-and-solution-treated 316LNss after short-term oxidation (190 h) in high-temperature high-pressure water for nuclear power applications. The results demonstrate that forging and post-forging solution treatment can refine grain size and reduce residual strain, while simultaneously eliminating the texture present in the as-received 316LNss. The oxide film generated on the 316LNss surface in high-temperature high-pressure water exhibits a duplex characteristic; the outer oxide film comprises hydroxides and Fe-rich spinel-structured oxides, whereas the inner oxide film consists primarily of Cr-rich spinel-structured oxides. Compared with the as-received 316LNss, the forged-and-solution-treated 316LNss develops a thinner oxide film with higher Cr content and a lower oxidation rate. Finally, the oxidation mechanism of 316LNss in high-temperature high-pressure water is discussed.

Full Text

Short-term Oxidation Behavior of Forged 316LN Stainless Steel in High-Temperature Pressurized Water

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Abstract: The effects of forging and post-forging solution annealing on the average grain size, residual strain, and grain orientation distribution of nuclear-grade 316LN austenitic stainless steel (316LNss) were investigated using electron backscatter diffraction (EBSD). The morphology and chemical composition of oxide films formed on both as-received and forged-plus-solution-annealed 316LNss after short-term oxidation (190 h) in simulated nuclear reactor high-temperature pressurized water were also analyzed. The results demonstrate that forging followed by solution annealing effectively reduced grain size, eliminated residual strain, and removed crystallographic texture present in the as-received material. A duplex oxide film developed on 316LNss surfaces in high-temperature pressurized water, consisting of an outer layer of hydroxides and Fe-enriched spinel oxides and an inner layer predominantly composed of Cr-enriched spinel oxides. Compared with as-received 316LNss, the forged and solution-annealed material exhibited a lower oxidation rate, forming a thinner oxide film with higher chromium content. The oxidation mechanism is discussed in detail.

Keywords: material failure and protection, 316LN stainless steel, oxide film, high-temperature pressurized water, forging, corrosion, nuclear power

Introduction

Stainless steels and nickel-based alloys, as structural materials in nuclear power systems, undergo oxidation as the most fundamental form of corrosion when exposed to high-temperature, high-pressure water environments in light water reactors (pressurized water reactors and boiling water reactors) and heavy water reactors. This oxidation process underlies other environmentally assisted failure mechanisms such as stress corrosion cracking (SCC) [1, 2]. Several SCC models —including the slip-oxidation/film-rupture model [3], the coupled-environment fracture model [4], and the internal oxidation model [5]—all indicate that metal oxidation behavior critically influences SCC susceptibility. Furthermore, the radioactivity in pressurized water reactor (PWR) primary coolant is largely determined by corrosion-released ions from system components [6]. Studies of metal oxidation also guide the development of corrosion prevention strategies. For example, zinc injection in PWR primary water enhances plant efficiency and service life, partly by promoting the formation of more compact and protective oxide films [7, 8]. Therefore, investigating metal oxidation behavior in high-temperature pressurized water is of significant importance.

Extensive research has been conducted on the oxidation behavior of stainless steels and nickel-based alloys in high-temperature water environments. Numerous studies [8-10] have shown that stainless steels develop a duplex oxide film in high-temperature water, with a Cr-enriched inner layer and an Fe-enriched outer layer. The structure and composition of these oxide films are influenced by multiple factors, including water chemistry parameters [11, 12] (dissolved oxygen, dissolved hydrogen, pH, etc.), microstructural characteristics [13, 14] (grain size, grain boundary structure, etc.), and stress/strain states [15, 16].

Metal processing (hot and cold working) alters microstructure, thereby affecting oxidation behavior. Cold working has been shown to increase corrosion and SCC susceptibility in high-temperature water [10, 16-18]. Féron et al. [10] found that cold-worked metals develop discontinuous inner oxide films with reduced protective capability compared to non-cold-worked materials. To enhance overall quality, third-generation AP1000 nuclear power plants utilize integrally forged 316LNss for main coolant piping. While numerous studies have examined the effects of forging on stainless steel microstructure and mechanical properties [19, 20], research on the corrosion and SCC behavior of forged stainless steel in nuclear reactor environments remains limited [21], necessitating further investigation into the oxidation mechanisms of forged stainless steel in high-temperature pressurized water.

1 Experimental Methods

1.1 Material and Sample Preparation

The chemical composition of the 316LNss used in this study is presented in . As-received (non-forged) material was multi-directionally forged at 1130°C with a forging ratio of 6, followed by solution treatment at 1070°C for 10 h to eliminate residual stresses and strains, with water cooling. This heat treatment mirrors the actual process used for nuclear reactor coolant piping. The forged and solution-treated material is hereafter referred to as "forged 316LNss." All test samples measured 10 mm × 10 mm × 1 mm.

For EBSD analysis, samples were ground to 2000-grit, mechanically polished with 2.5 m and 1.5 m diamond paste, and finally electropolished in a solution of 20% $HClO_4$ + 80% CH_3COOH (by volume) at 25 V DC, 2 A for 20-25 s. EBSD scans were performed using an FEI XL30FEG scanning electron microscope (SEM) with the sample stage tilted 70° to the horizontal plane and a scan step size of 7 m. The acquired data were analyzed using OIM (orientation imaging microscopy) software from TSL.

For corrosion testing, samples were drilled at the edges for suspension, ground to 2000-grit, mechanically polished with 2.5 m diamond paste, ultrasonically cleaned, and dried. Immersion tests were conducted in a dynamic high-temperature pressurized water circulation system constructed from 316L stainless steel. The water chemistry contained 1500×10^{-6} B (as H_3BO_3) and 2.3×10^{-6} Li (as $LiOH \cdot H_2O$) by mass fraction. High-purity nitrogen was purged before heating to reduce dissolved oxygen to $<1 \times 10^{-9}$ by volume fraction. Test conditions were 300°C and 10 MPa pressure, with an isothermal hold time of 190 h (excluding heating and cooling periods). After removal, samples were blotted dry with filter paper, placed in a desiccator, and promptly analyzed.

1.2 Characterization Methods

Surface oxide film morphology was examined by SEM, and chemical composition was analyzed by energy-dispersive spectroscopy (EDS). Phase identification of surface oxides was performed using a D/Max-2400 X-ray diffractometer (XRD) with Cu Kα radiation at 40 kV and a scanning step of 0.05°. Chemical composition and depth profiles of oxide films were determined using an ESCALAB 250 X-ray photoelectron spectrometer (XPS) with Al Kα excitation (1486.6 eV, 150 W, pass energy 50.0 eV). Depth profiling was conducted by Ar^+ sputtering over a 2 mm × 2 mm area, with signal collection from a 0.5 mm diameter spot. The sputtering rate was $0.1\ \text{nm} \cdot \text{s}^{-1}$ (relative to Ta_2O_5). Elemental information was recorded at various sputtering depths. Ni $2p_2/_3$, Cr $2p_2/_3$, Fe $2p_2/_3$, and O 1s spectra were deconvoluted using XPSPEAK 4.1 software with Gaussian-Lorentzian peak shapes and Shirley backgrounds. Peak positions were calibrated using the C 1s peak at 285.0 eV. Elemental valence states and possible compounds were identified based on literature data [22], summarized in .

2 Results and Discussion

2.1 Microstructure and Residual Strain

shows the chemical composition of 316LNss. [Figure 1: see original paper] presents EBSD results for both as-received and forged materials. The grain average misorientation (GAM) parameter, which characterizes residual strain magnitude and distribution, reveals that forged 316LNss exhibits lower and more uniformly distributed residual strain. Black lines in [Figure 1: see original paper]a and c represent grain boundaries. Statistical analysis indicates average grain sizes of 463.572 m for as-received and 147.201 m for forged 316LNss. As a single-phase austenitic stainless steel, solution treatment alone cannot refine grain size, whereas forging effectively reduces it. Pole figure (PF) analysis shows uniform grain orientation without obvious texture in the forged material, while the as-received material exhibits orientation clustering that is detrimental to mechanical properties ([Figure 1: see original paper]b and d).

Forging of 316LNss was conducted above the recrystallization temperature, inducing recrystallization where strain-free equiaxed grains replace original coarse deformed grains, resulting in significant grain refinement and residual strain reduction [20]. Solution treatment further decreases internal residual strain.

2.2 Oxide Film Morphology

[Figure 2: see original paper] shows SEM images of oxide films formed on both material conditions after 190 h immersion. The outermost oxide layer on both samples consists of randomly distributed polyhedral oxide particles, with no significant morphological differences. The images clearly reveal a duplex film structure [7]: large oxide particles constitute the outer layer, while a dense inner oxide layer resides beneath these particles.

Due to the relatively short exposure time (190 h), oxide particles have not yet formed a complete coverage. Consequently, no pronounced differences in particle size or distribution are observed between the two conditions, necessitating further analysis of chemical composition and effective thickness. Outer layer particle sizes range from approximately 100 nm to 800 nm. lists SEM-EDS results for four representative particles (A1, A2, B1, B2) marked in [Figure 2: see original paper]. The similar compositions of these particles, and their consistency with other large oxide particles, indicate that forging does not significantly affect oxide particle chemistry.

2.3 Chemical Composition of Oxide Films

XRD analysis ([Figure 3: see original paper]) reveals that oxide films on both samples consist primarily of spinel-structure oxides M_3O_4 (M = Ni, Cr, Fe), such as $FeCr_2O_4$ and Fe_3O_4. However, the thin film thickness and small differences in 2 angles among these spinel oxides [23] preclude definitive phase identification. Other studies have similarly identified spinel phases as long-term corrosion products of stainless steel in high-temperature water [10, 11, 24]. Furthermore, E-pH diagrams for the Ni-Cr-Fe-H_2O system at 300°C [25] indicate that spinel-structure oxides are thermodynamically stable on 316LNss surfaces under these conditions.

XPS depth profiling results are presented in [Figure 4: see original paper]. The oxide/metal interface was defined as the depth where oxygen content decreased to 50% of its initial value at 0 s sputtering time. Sputtering times to reach this interface were 507 s for as-received and 374 s for forged 316LNss, indicating a thicker oxide film on the as-received material. Integrated composition calculations ([Figure 5: see original paper]) show that the forged 316LNss oxide film contains higher Cr and lower Fe concentrations compared to the as-received condition, while Ni contents are similar. Higher Cr content corresponds to increased Cr-rich spinel oxide or Cr_2O_3 formation, resulting in more protective films and lower corrosion rates [26].

Detailed XPS spectra of Cr $2p_3/_2$ are shown in [Figure 6: see original paper]. At 0 s and 30 s sputtering times, two main peaks are observed: one corresponding to Cr^{3+} in CrOOH and another to Cr(III) in spinel oxides or Cr_2O_3, with higher Cr(III) content at 30 s. At 400 s, three peaks appear: CrOOH, Cr(III), and Cr^0. With increasing sputtering time, CrOOH content decreases while Cr^0 content increases, indicating approach to the substrate. The maximum Cr(III) content at 400 s confirms that Cr exists primarily as spinel oxides or Cr_2O_3 in the inner layer. The forged sample exhibits higher Cr(III) content than the as-received material, indicating a greater proportion of Cr-rich spinel oxides or Cr_2O_3. At

1650 s sputtering time, Cr exists mainly as Cr^0 and Cr(III).

Ni $2p_3/_2$ spectra ([Figure 7: see original paper]) show that at 0 s sputtering, Ni exists primarily as $Ni(OH)_2$ and Ni(II) (corresponding to Ni-containing spinel oxides such as $NiFe_2O_4$ and $NiCr_2O_4$). The Ni^0 peak appears at 30 s due to reduction of nickel oxides by Ar^+ bombardment. With increasing depth, Ni^0 content increases while $Ni(OH)_2$ decreases. At 400 s and 1650 s, Ni exists as both Ni^0 and Ni(II), with Ni^0 predominating, indicating that the substrate is reached by 400 s. At 30 s sputtering, the as-received sample contains more $Ni(OH)_2$ than the forged sample, reflecting its greater oxide film thickness (see Section 2.5).

2.4 Oxidation Mechanism

Fe $2p_3/_2$ spectra ([Figure 8: see original paper]) reveal that at 0 s sputtering, Fe exists primarily as Fe^{3+} with minor Fe^{2+}, possibly corresponding to Fe_3O_4 or FeOOH [27]. At 30 s, two distinct peaks correspond to Fe^{3+} and Fe^{2+}, with Fe^{2+} content significantly increased. At 400 s, a pronounced Fe^0 peak indicates proximity to the substrate. Notably, Fe^{3+} persists at 400 s in the as-received sample, confirming that the oxide/metal interface has not been fully reached, consistent with a thicker oxide film. In contrast, the forged sample at 400 s shows Fe mainly as Fe^0 and Fe^{2+}. Combined with XRD results ([Figure 3: see original paper]), this indicates that Fe in the inner layer exists primarily as spinel oxides ($Fe(Cr,Ni)_2O_4$).

O 1s spectra at various sputtering depths ([Figure 9: see original paper]) show that oxygen exists as both O^{2-} and OH^-, with their relative proportions varying with depth. Generally, OH^- content decreases while O^{2-} content increases with sputtering time.

The outer layer of stainless steel oxide films in high-temperature water grows via a metal dissolution and oxide precipitation mechanism, while the inner layer grows via a solid-state mechanism [27, 28]. XPS results ([FIGURE:6-9]) show hydroxides concentrated at the outer surface. Combined with SEM and SEM-EDS data ([Figure 2: see original paper] and), these findings confirm the duplex structure of 316LNss oxide films ([Figure 10: see original paper]) [29, 30].

Oxidation in high-temperature water is fundamentally electrochemical, as water dissociates into H^+ and OH^- [27, 29]. During initial oxidation, oxygen diffuses into the substrate along grain boundaries and dislocations. Due to Cr' s highest oxygen affinity, it oxidizes preferentially, with remaining oxygen subsequently reacting with Ni and Fe. This is followed by oxide particle growth and dissolution, constituting oxide film formation [31]. Diffusion rates in oxides follow the order Fe > Ni » Cr, causing Cr to oxidize and stabilize in the inner layer, gradually forming Cr-rich spinel oxides [11, 23, 28]. Thermodynamic calculations and crystallographic analysis suggest that stainless steel in deoxygenated high-temperature water forms Fe_3O_4 outer layer and $FeCr_2O_4$ inner layer [8, 25], consistent with other studies [9, 32]. Based on XRD, XPS, and literature

[8, 9, 25, 32], the inner layer of 316LNss oxide film in high-temperature water consists primarily of $FeCr_2O_4$, while the outer layer comprises $(Ni,Fe)Fe_2O_4$, with metastable Fe_3O_4 possibly precipitating from dissolved Fe ions in solution [33].

Spinel oxides have an oxygen close-packed structure with the general formula AB_2O_4, where O atoms are cubic close-packed on (111) planes and A/B cations occupy tetrahedral (12.5%) and octahedral (25%) interstices. The diffusion capacity of metal ions (Fe, Ni, Cr) in the spinel lattice governs the oxidation rate. The effect of forging on 316LNss oxidation rate can be analyzed from the perspective of metal ion and oxygen diffusion. XPS analysis shows that forged 316LNss forms a thinner oxide film with higher Cr(III) content and lower corrosion rate after 190 h immersion in simulated PWR primary water. The primary reasons are: (1) **Grain size effect**: Bulk diffusion is much slower than grain boundary diffusion, and Cr' s high oxygen affinity makes grain boundaries preferential nucleation sites for Cr(III) oxides. The forged material' s smaller grain size provides more grain boundaries, promoting Cr diffusion. The higher density of Cr(III) oxide nucleation sites leads to a more compact inner layer that reduces outward metal ion diffusion and inward oxygen diffusion, suppressing outer layer growth and decreasing corrosion rate [13]. (2) **Residual strain effect**: Higher residual strain in as-received 316LNss corresponds to greater defect density (e.g., dislocations), providing more rapid diffusion pathways that increase corrosion rates [16]. Féron et al. [10] observed that cold-worked 316L stainless steel with high residual strain formed discontinuous inner oxide films with poor protectiveness, while annealed 316L formed continuous inner layers that effectively inhibited further oxidation.

It should be noted that the oxidation behavior differences between as-received and forged 316LNss result from combined effects of grain size, residual strain, and other factors. While this study cannot definitively identify the dominant factor, it clearly demonstrates that forged 316LNss exhibits superior oxidation resistance in high-temperature pressurized water. These results indicate that forged main coolant piping (with post-forge solution treatment) enhances corrosion resistance in nuclear power plants.

3 Conclusions

1. Forging and post-forge solution treatment refine grain size, reduce residual strain, and eliminate crystallographic texture in 316LNss, removing the orientation clustering observed in as-received material.
2. After 190 h immersion in high-temperature pressurized water, 316LN stainless steel develops a duplex oxide film: an outer layer consisting of $Ni(OH)_2$ and other hydroxides plus Fe-rich spinel oxides, and an inner layer dominated by Cr-rich spinel oxides. The duplex structure likely arises from different nucleation and growth mechanisms for the inner and outer layers.
3. Compared with as-received 316LN stainless steel, the forged and solution-

annealed material forms a Cr-enriched, more protective oxide film, resulting in lower oxidation rates and thinner oxide films in high-temperature pressurized water.

References

1. J. Panter, B. Viguier, J. M. Cloué, M. Foucault, P. Combrade, E. Andrieu, Influence of oxide films on primary water stress corrosion cracking initiation of alloy 600, *Journal of Nuclear Materials*, 348(1), 213 (2006).
2. S. Wang, T. Shoji, N. Kawaguchi, Initiation of environmentally assisted cracking in high-temperature water, *Corrosion*, 61(2), 137 (2005).
3. S. M. Bruemmer, L. E. Thomas, Insights into stress-corrosion cracking mechanisms from high-resolution measurements of crack-tip structures and compositions, in: *MRS Proceedings*, edited by J. K. Gibson, S. K. McCall, E. D. Bauer, L. Soderholm, T. Fanghaenel, R. Devanathan, A. Misra, C. Trautmann, B. D. Wirth (UK, Cambridge University Press, 2010) P. 1264-BB01-09.
4. D. D. MacDonald, M. Urquidi-MacDonald, A coupled environment model for stress corrosion cracking in sensitized type 304 stainless steel in LWR environments, *Corrosion Science*, 32(1), 51 (1991).
5. R. B. Rebak, Z. Szklarska-Smialowska, The mechanism of stress corrosion cracking of alloy 600 in high temperature water, *Corrosion Science*, 38(6), 971 (1996).
6. M. Bojinov, A. Galtayries, P. Kinnunen, A. Machet, P. Marcus, Estimation of the parameters of oxide film growth on nickel-based alloys in high-temperature water electrolytes, *Electrochimica Acta*, 52(26), 7475 (2007).
7. X. Liu, X. Wu, E.-H. Han, Effect of Zn injection on established surface oxide films on 316L stainless steel in borated and lithiated high temperature water, *Corrosion Science*, 65, 136 (2012).
8. X. Liu, X. Wu, E.-H. Han, Electrochemical and surface analytical investigation of the effects of Zn concentrations on characteristics of oxide films on 304 stainless steel in borated and lithiated high temperature water, *Electrochimica Acta*, 108, 554 (2013).
9. Y. Soma, C. Kato, M. Yamamoto, Multilayered surface oxides within crevices of Type 316L stainless steels in high-temperature pure water, *Corrosion*, 70(4), 366 (2014).
10. D. Féron, E. Herms, B. Tanguy, Behavior of stainless steels in pressurized water reactor primary circuits, *Journal of Nuclear Materials*, 427(1), 364 (2012).
11. X. Liu, E.-H. Han and X. Wu, Effects of pH value on characteristics of oxide films on 316L stainless steel in Zn-injected borated and lithiated

high temperature water, *Corrosion Science*, 78, 200 (2014).

12. W. Kuang, X. Wu and E.-H. Han. Influence of dissolved oxygen concentration on the oxide film formed on Alloy 690 in high temperature water, *Corrosion Science*, 69, 197 (2013).
13. J. Kim, D. Kim, S. Suwas, E. Fleury, K. Yi, Grain-size effects on the high-temperature oxidation of modified 304 austenitic stainless steel, *Oxidation of Metals*, 79(3), 239 (2013).
14. S. Lozano-Perez, K. Kruska, I. Iyengar, T. Terachi, T. Yamada, The role of cold work and applied stress on surface oxidation of 304 stainless steel, *Corrosion Science*, 56, 78 (2012).
15. J. Hou, T. Shoji, Z. P. Lu, Q. J. Peng, J. Q. Wang, E.-H. Han, W. Ke, Residual strain measurement and grain boundary characterization in the heat-affected zone of a weld joint between Alloy 690TT and Alloy 52, *Journal of Nuclear Materials*, 397(1), 109 (2010).
16. S. Perrin, L. Marchetti, C. Duhamel, M. Sennour, F. Jomard, Influence of irradiation on the oxide film formed on 316L stainless steel in PWR primary water, *Oxidation of Metals*, 80(5), 623 (2013).
17. J. Hou, T. Shoji, Z. P. Lu, Q. J. Peng, J. Q. Wang, E.-H. Han, W. Ke, Environmentally assisted crack growth in one-dimensionally cold worked Alloy 690TT in primary water, *Corrosion Science*, 57, 81 (2012).
18. H. Sun, X. Wu, E.-H. Han, Y. Wei, Effects of pH and dissolved oxygen on electrochemical behavior and oxide films of 304SS in borated and lithiated high temperature water, *Corrosion Science*, 59, 334 (2012).
19. T. Sakai, A. Belyakov, R. Kaibyshev, H. Miura, J. J. Jonas, Dynamic and post-dynamic recrystallization under hot, cold and severe plastic deformation conditions, *Progress in Materials Science*, 60, 130 (2014).
20. Y. Cao, H. Di, J. Zhang, J. Zhang, T. Ma, R. D. K. Misra, An electron backscattered diffraction study on the dynamic recrystallization behavior of a nickel-chromium alloy (800H) during hot deformation, *Materials Science and Engineering A*, 585, 71 (2013).
21. L. Zhang, J. Q. Wang, E.-H. Han, Stress corrosion crack growth behavior of domestic forged nuclear-grade 316L stainless steel pipe in high-temperature high-pressure water, *Acta Metallurgica Sinica*, 49(08), 911 (2013).
22. J. F. Moulder, F. S. William, E. S. Peter, *Handbook of X-ray Photoelectron Spectroscopy* (USA, Perkin-Elmer Corporation, 1992) p. 1264-BB01-09.
23. Z. Zhang, J. Q. Wang, E.-H. Han, Characterization of different surface states and its effects on the oxidation behaviours of Alloy 690TT, *Journal of Materials Science and Technology*, 28(4), 353 (2012).

24. S. Perrin, L. Marchetti, C. Duhamel, M. Sennour, F. Jomard, Influence of irradiation on the oxide film formed on 316L stainless steel in PWR primary water, *Oxidation of Metals*, 80(5), 623 (2013).
25. X. Liu, X. Wu, E.-H. Han, Effect of Zn injection on established surface oxide films on 316L stainless steel in borated and lithiated high temperature water, *Corrosion Science*, 65, 136 (2012).
26. P. Marcus, J. M. Grimal, The anodic dissolution and passivation of NiCrFe alloys studied by ESCA, *Corrosion Science*, 33(5), 805 (1992).
27. B. Stellwag, The mechanism of oxide film formation on austenitic stainless steels in high temperature water, *Corrosion Science*, 40(2), 337 (1998).
28. N. K. Das and T. Shoji, Early stage oxidation initiation at different grain boundaries of fcc Fe-Cr binary alloy: a computational chemistry study, *Oxidation of Metals*, 79(3), 429 (2013).
29. F. Huang, J. Q. Wang, E.-H. Han, W. Ke, Short-time oxidation of Alloy 690 in high-temperature and high-pressure steam and water, *Journal of Materials Science and Technology*, 28(6), 562 (2012).
30. V. A. Ignatova, S. Van Dyck, R. Grötzschel, W. Möller, XPS depth profiling of oxide scales of stainless steels formed in high-temperature aqueous conditions, *Surface and Interface Analysis*, 38(4), 396 (2006).
31. M. Bojinov, A. Galtayries, P. Kinnunen, A. Machet, P. Marcus, Estimation of the parameters of oxide film growth on nickel-based alloys in high-temperature water electrolytes, *Electrochimica Acta*, 52(26), 7475 (2007).
32. X. Liu, X. Wu, E.-H. Han, Influence of Zn injection on characteristics of oxide film on 304 stainless steel in borated and lithiated high temperature water, *Corrosion Science*, 53(10), 3337 (2011).
33. X. Liu, X. Wu, E.-H. Han, Effect of Zn injection on established surface oxide films on 316L stainless steel in borated and lithiated high temperature water, *Corrosion Science*, 65, 136 (2012).

Note: Figure translations are in progress. See original paper for figures.