# pH agent effect on corrosion behavior of 316L Stainless Steel in Boron-free High-Temperature Water

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## 1. Introduction

Nuclear power plants (NPPs) are acknowledged as a potential solution for mitigating air pollution and addressing climate change, as it produces electricity in an environmentally friendly manner while ensuring stable and reliable energy production. There is a growing interest in the development of Small Modular Reactors (SMRs), which have a maximum power output below 300 MW, and can be used for coal replacement, distributed power, hydrogen production, etc. Currently, more than 70 SMR designs are being developed in 16 countries worldwide, with 31 of them adopting a pressurized water reactor design that uses water as a coolant [1].

Recently, South Korea has also been actively developing the innovative SMR (i-SMR) by adopting boron-free coolant water chemistry [2,3]. The boronfree core design offers several advantages, such as reducing the amount of liquid radioactive waste, mitigating crud induced power shift (CIPS), and simplifying the chemical and volume control system (CVCS) used to regulate boron concentration. In addition, the use of potassium hydroxide (KOH) is being explored as an alternative pH control agent for the primary water chemistry, as it offers advantages in terms of both price and supply compared to the previously used lithium hydroxide (LiOH).

The Electric Power Research Institute (EPRI) has carried out extensive research to explore the use of KOH as a replacement for LiOH, which is a pH control agent for the primary water chemistry in commercial pressurized water reactors (PWRs) [4]. The VVER, which operates in Russia, has verified that Zr-alloy fuel cladding has good corrosion resistance in a water chemistry environment where KOH is used as the pH control agent [5,6]. Most recently, Kai Chen et al. [7] found that replacing LiOH with KOH as a pH control agent in simulated PWR primary water had no significant effect on the irradiation-assisted stress corrosion cracking (IASCC) crack growth rate of the 304 stainless steel (SS). However, research on the corrosion characteristics of 316L SS as an i-SMR structural materials in boron-free environment has not been extensively conducted.

Therefore, in this study, the corrosion behavior of 316L SS was investigated in a simulated boron-free

primary water environment with two different pH control agents. After the immersion test, the corrosion rate was measured, and the oxide products were also analyzed using surface analysis tools.

# 2. Experimental

## 2.1 Test material and conditions

The test material used in this study is commercial 316L SS which is considered for use in piping, valves and pumps for i-SMR. The chemical composition of the alloy used in this study is shown in Table 1.

Table 1: Chemical composition of 316L SS (wt.%)

С	Ni	Cr	Fe
0.016	10.08	16.22	Bal.
Mo	Mn	Р	S
2.05	1.03	0.03	0.002

316L SS was cut by electro-discharge machining into 10 mm  $\times$  25 mm  $\times$  2 mm specimens. The edges of the specimens were mechanically ground using 400 grit silicon carbide paper. All surfaces were mechanically polished with colloidal silica suspension down to 0.04  $\mu$ m. Then, all specimens were ultrasonically cleaned with acetone, ethanol, and distilled water in sequence.

The corrosion test was conducted in an autoclave equipped with a high temperature water loop circulation system. Specimens were exposed for up to 2000 hours.

The test solution was prepared by adding 0.27 ppm LiOH or 1.49 ppm KOH into high-purity water and subsequently adjusting the pH to 7.2 at  $320^{\circ}$ C.

Before raising the temperature, the solution was deaerated by purging with pure argon (Ar) gas to reduce the dissolved oxygen (DO) concentration to below 5 ppb. Subsequently, pure hydrogen (H<sub>2</sub>) gas was continuously injected to maintain a dissolved hydrogen (DH) concentration of 25 cc/kg·H<sub>2</sub>O. The test was carried out under the conditions of a temperature of  $320^{\circ}$ C and a pressure of 150 bar.

# 2.2 Chemical descaling methodology

The chemical descaling methodology was used to determine the corrosion rate of 316L SS. To remove corrosion products from the oxidized specimens, a twostep alkaline permanganate and ammonium citrate descaling process was repeatedly applied. The oxidation step involved immersing the specimens in a solution of 1% potassium permanganate (KMnO<sub>4</sub>) and 5% sodium hydroxide (NaOH), followed by the dissolution step in a 5% diammonium citrate solution. Each step was conducted by immersing the specimens in a water bath at 90°C for 5 minutes. After both steps were completed, the specimens were weighed. The weight at which the oxide film was completely removed from the specimens was determined through several repetitions, and the corrosion rate was calculated using the following equation (1):

Corrosion rate 
$$(mg/dm^2h) = (W_i - W_d) / (A \times T)$$
 (1)

where,  $W_i$  is the mass of the specimen before the corrosion test [mg];  $W_d$  is the descaled mass of the specimen [mg]; A is the surface area of the specimen [dm<sup>2</sup>]; T is the test time (h).

# 2.3 Microstructure characterizations

The surface of specimens was observed by field emission scanning electron microscopy (FE-SEM, Mira3, Tescan) at 15 kV. The crystal structures were analyzed by X-ray diffraction (XRD, Ultima IV, Rigaku) using Cu-K $\alpha$  radiation at 40 kV/20 mA. The cross sections of the oxide films were examined by transmission electron microscope (TEM, JEM-ARM200F) equipped with an energy dispersive spectrometer (EDS) system operating at 200 kV. The TEM specimens were prepared by using a dual-beam focused ion beam (DB-FIB, FEI Scios) with Ga ion sputtering after a protective Pt layer was deposited on the selected oxide films.

## 3. Results and Discussion

# 3.1 Corrosion rate by chemical descaling

The corrosion rates of 316L SS specimens after the corrosion test are shown in Fig. 1 as a function of time. During the initial 250 hours, the corrosion rate is relatively high. However, as exposure time increases, the corrosion rate rapidly decreases initially and then stabilizes. This behavior indicates that oxidation in a simulated boron-free primary water environment leads to the gradual formation of a passive film, which progressively improves the corrosion resistance of 316L SS over time. When compared to the boron-free ammonia environment investigated by Shim et al. [8], the corrosion rates in the LiOH and KOH environments remain consistently lower throughout the entire

exposure period. Additionally, in comparison to the conventional PWR primary water conditions reported by Esposito et al. [9], which contain boric acid (H<sub>3</sub>BO<sub>3</sub>) and LiOH, the corrosion rate in the boron-free LiOH or KOH environments is expected to reach a similar level if the exposure time extends to 2500 hours.

Overall, these results demonstrate that boron-free primary water environments with LiOH or KOH provide long-term corrosion resistance comparable to PWR primary water environment.



Fig. 1. Corrosion rate of 316L SS corroded in simulated boron-free primary water environments.

# 3.2 Oxide characteristics

Figure 2 shows SEM images of 316L SS surfaces after exposure to a simulated boron-free primary water environment at 320°C for 250 and 2000 hours, using LiOH or KOH as pH control agents. There are no significant differences in the surface morphology of 316L SS exposed to both environments. At 250 hours, polyhedral oxide particles formed on the surface, measuring approximately 2  $\mu$ m or smaller. As the exposure time increased to 2000 hours, the density of the polyhedral oxide particles increased, but their maximum size did not grow further. This oxide morphology is consistent with that observed in PWR primary water environments.



Fig. 2. SEM images of 316L SS surfaces after exposure to a simulated boron-free primary water environment for 250 or 2000 hours. (a) LiOH, (b) KOH.

Figure 3 presents the XRD patterns of 316L SS specimens after exposure to a simulated boron-free primary water environment. The diffraction patterns indicate that similar corrosion products formed on the surface, regardless of exposure times or pH control agents. The identified phases include  $Cr_2O_3$  and spinel oxides. The presence of  $Cr_2O_3$  suggests the possible formation of a protective chromium oxide layer, while spinel phases indicate the potential incorporation of iron, nickel, or chromium oxides, which are commonly observed in the alloy oxide formed in high-temperature water.



Fig. 3. XRD diffraction patterns of 316L SS exposed to boron-free primary water at 320°C for 250~2000 hrs.

The cross-sectional TEM analysis was conducted to examine the oxide layers formed on 316L SS after exposure to a boron-free primary water environment with LiOH or KOH. In both cases, the oxide layer exhibits a distinct double-layer structure, consisting of polyhedral outer oxide particles and an inner oxide layer. The outer oxide particles form through the precipitation of metal cations dissolved from the matrix, while the inner oxide layer develops via solid-state diffusion [10]. EDS mapping confirms the presence of an Fe-rich outer oxide and a Cr-enriched inner oxide. regardless of the pH control agent. Electron diffraction analysis further identifies Fe<sub>3</sub>O<sub>4</sub> in the outer layer, while the inner oxide is composed of a mixture of (Fe,Ni)(Fe,Cr)<sub>2</sub>O<sub>4</sub> spinel and Cr<sub>2</sub>O<sub>3</sub>. These results align with surface analysis findings from SEM and XRD shown in Figs. 2-3. Additionally, these findings indicate that the oxidation behavior in boron-free LiOH or KOH environments is nearly identical, with no significant differences in oxide structure.

Furthermore, the observed oxidation characteristics are quite similar to those reported in conventional PWR primary water environments [10]. This indicates that boron-free water chemistry preserves the fundamental oxidation mechanism of 316L SS, supporting its applicability in i-SMR primary water environments.

## **3.** Conclusions

This study examines the corrosion behavior of 316L stainless steel, a key structural material for i-SMRs, in a simulated boron-free primary water loop using LiOH or KOH as pH control agents. Corrosion performance was evaluated through corrosion rate measurement and oxide film characterization using SEM, XRD, and FIB-TEM. The key conclusions are as follows:

- The corrosion rate of 316L SS was initially high but gradually decreased and stabilized over time, reaching nearly the same value after approximately 2000 hours.
- Polyhedral oxide particles, approximately 2 µm or smaller, were observed on the surface. As the exposure time increased, the density of these particles increased, while their maximum size remained unchanged.
- XRD confirmed the formation of Cr<sub>2</sub>O<sub>3</sub> and spinel oxides, while TEM-EDS identified the outer layer as Fe<sub>3</sub>O<sub>4</sub> particles and the inner layer as a mix of (Fe,Ni)(Fe,Cr)<sub>2</sub>O<sub>4</sub> spinel and Cr<sub>2</sub>O<sub>3</sub>.
- No significant differences in the corrosion behavior of 316L SS were observed between LiOH and KOH environments, and the overall oxidation behavior was quite similar to that of conventional PWR primary water conditions.

This study is expected to serve as essential corrosion data supporting the long-term durability and safety of i-SMR.

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