

Accelerated Oxidation of Stainless Steels in Heavy-Water Reactor Spent Fuel Pool Accidents

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1. Introduction

Spent nuclear fuel from heavy-water reactors is stored on racks in spent fuel pools at reactor sites after discharge to allow for radioactive decay and cooling. These pools consist of water-filled tanks, and the storage racks are constructed from stainless steel to ensure structural integrity. To maximize storage efficiency, high-density racks are commonly employed. In the event of an accidental coolant leakage, the spent fuel can overheat, causing the surrounding water to boil and generate a high-temperature steam atmosphere. Additionally, the racks themselves experience a temperature increase due to prolonged contact with the overheated spent fuel, further exacerbating the risk of oxidation and structural degradation. Under such conditions, 304 stainless steel, the primary material used for these racks, may undergo rapid oxidation, potentially resulting in structural failure or collapse. This study investigates the high-temperature oxidation behavior of 304 stainless steel under these simulated accident conditions.

2. Experimental

The composition of the SS304H specimen is presented in Table 1. The specimens used in this study had dimensions of 8mm x 20mm x 3.5mm, with a small hole of 1.5 mm diameter near one edge as shown in Fig. 1a. Before oxidation experiments, all samples were polished to 1 μ m, washed in acetone, and rinsed with ethanol.

304H	Cr	Ni	Si	Mn	Si	C	P
wt%	20	10.5	0.03	2.0	0.75	0.1	0.045

Table 1. Chemical composition of SS304H

To simulate the high-temperature exposure of SS 304H specimens in a steam atmosphere, an induction heating-based experimental setup, designed in-house, was used to perform thermogravimetric analysis (TGA). The experimental setup, as shown in Fig. 1b, consisted of an induction heater, a pyrometer for temperature measurement, a microbalance for automatically recording the weight change of the specimens over time, and a steam generation and flow control system. Each component was efficiently positioned to ensure the accuracy and reproducibility of the experiments.

Oxidation experiments were conducted in both air and steam atmospheres at temperatures ranging from 800 to

1000°C for two hours. The air and steam atmospheres were composed of natural air from inside the laboratory.

The experimental setup, adopting an induction heating method, was designed to reach the target temperatures within one minute and was optimized for rapid heating. The reliability of the induction heating device was verified by comparing temperatures from the thermocouple and pyrometer to calibrate the experimental temperatures, and appropriate induction currents were applied to achieve the pre-defined specimen temperature. The specimen was connected to a chromel wire and positioned in the center of the induction coil inside a vertical quartz tube, and the weight change was automatically recorded every second by an AND GH-202 microbalance with a resolution of 10⁻⁴ g, linked to a computer.

Steam was generated by heating water in a flask to over 100°C on a hot plate and continuously injected into a vertical quartz tube at a flow rate of 2.5 ml/min. To maintain a consistent temperature and prevent steam condensation, the pipe of the experimental setup was wrapped with heating tape. The injected steam was expelled externally through an exhaust fan. Air-atmosphere experiments were conducted without steam injection. After two hours of exposure, the specimens were air-cooled to room temperature in a crucible.

The oxidized specimens were analyzed using Scanning Electron Microscopy (SEM), Energy-Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD) to investigate their structure and composition

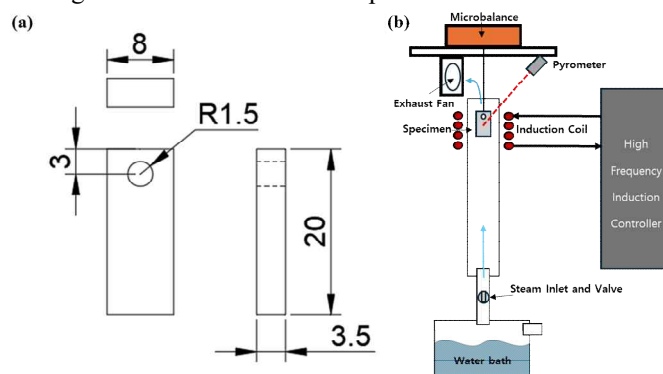


Fig. 1. (a) Experimental sample dimensions (unit: mm), (b) Schematic diagram of the high-frequency induction heating experimental setup

3. Result and Discussion

3.1 Weight Gain Behavior and Oxidation Kinetics

Figure 2 presents the continuous measurement of weight changes in the specimens during oxidation. The results indicate that oxidation is significantly accelerated in a steam atmosphere, leading to a greater weight gain compared to an air atmosphere. Additionally, with increasing temperature, the oxidation behavior transitions from a linear to a parabolic trend, suggesting a saturation in the oxidation rate. This shift suggests that as oxidation progresses, the growth of oxide layers may influence further oxidation kinetics, possibly due to changes in diffusion pathways or oxide scale stability.

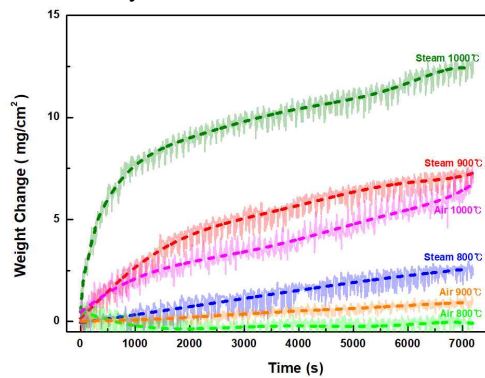


Fig. 2. TGA curves of the SS 304H sample oxidized at 800-1000°C for 2h.

3.2 Comparison with Fe-Based Alloys and Heating Methods

Figure 3 compares the high-temperature oxidation behavior observed in this study with previously reported results for Fe-based alloys. Unlike conventional oxidation experiments conducted using TGA or tube furnaces, this study employed an induction heating system to simulate direct and rapid heating conditions. A key distinction from conventional TGA experiments is that only the specimen was heated in an open environment, rather than the entire atmosphere being uniformly heated. Notably, the weight gain of SS304 oxidized in an air atmosphere using conventional TGA was lower than that observed in this study under similar conditions, suggesting that heating in an open environment enhances oxidation kinetics. The rapid heating and cooling cycles associated with induction heating may contribute to increased oxidation rates by promoting the formation and growth of oxide layers in a non-equilibrium state.

3.3 Formation of Fe-Rich Islands

K. A. Habib et al. [5] reported the presence of Fe-rich islands and a damaged chromia layer on the surface of oxidized specimens. Notably, Fe-rich islands in their study were observed after 100 hours of oxidation at

1000°C, with a corresponding weight gain of approximately 16 mg/cm². However, as shown in Fig. 4, Fe-rich islands were detected in this study after only 2 hours of oxidation, even at 800°C (Fig. 4a), with significantly larger islands forming at 1000°C (Fig. 4b).

Given the substantial difference in exposure time between this study and that of [5], it is suggested that Fe-rich islands play a critical role in the observed weight gain. Remarkably, the weight gain observed in this study after just 2 hours of oxidation at 1000°C (approximately 7 mg/cm²) already accounts for nearly half of the 100-hour oxidation weight gain reported by [5]. This suggests that Fe diffusion and oxide formation occur at a much faster rate, leading to accelerated mass gain. The presence of Fe-rich islands at such an early stage of oxidation indicates that they contribute significantly to the high-temperature oxidation process by locally disrupting the protective chromia layer, thereby promoting further oxidation.

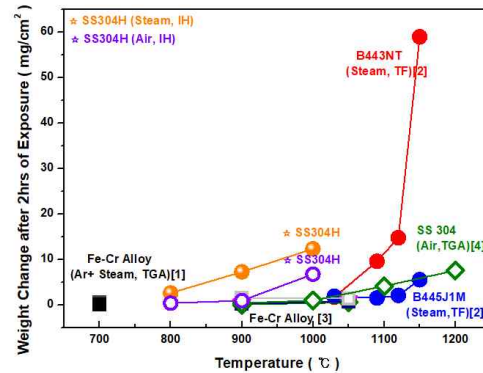


Fig. 3. High-Temperature Oxidation Behavior of Alloys: Reference [1,2,3,4] and Experimental Data

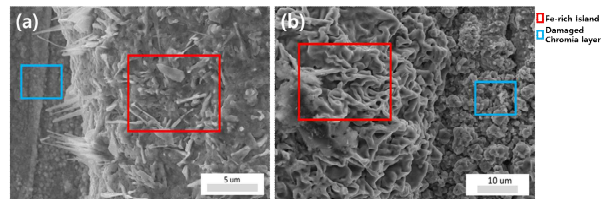


Fig. 4. SEM micrograph of the surface of SS304H oxidized in air for 2 hours; (a) at 800°C, (b) at 1000°C

4. Conclusion

In this study, the oxidation behavior of SS304H was investigated in both air and steam atmospheres at temperatures ranging from 800 to 1000°C using an induction heating system. The key findings are as follows:

- (1) Oxidation kinetics were significantly accelerated in the steam atmosphere compared to the air atmosphere. As the temperature increased, the oxidation behavior transitioned from a linear to a parabolic trend, indicating saturation. This suggests that the formation and growth of oxide layers influence oxidation kinetics,

likely by changing diffusion pathways or affecting oxide scale stability.

(2) Compared to oxidation behaviors reported in previous studies using TGA and tube furnaces for Fe-based alloys, the direct and rapid heating conditions of the induction heating method used in this study, along with the open experimental setup, resulted in an increased oxidation rate.

(3) Fe-rich islands and a damaged chromia layer, previously observed after 100 hours at 1000°C with a weight gain of ~16 mg/cm², were detected in this study after only 2 hours, even at 800°C. At 1000°C, the weight gain reached ~7 mg/cm², nearly half of the 100-hour value, indicating rapid Fe diffusion and oxidation. The size of Fe-rich islands increased with temperature, suggesting their significant contribution to the accelerated mass gain.

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