

Corrosion and Release Behaviors of Stainless Steel 316L in Boron-Free Primary Coolant

Hee-Sang Shim*, Soon-Hyeok Jeon, Do Haeng Hur

*Materials Safety Technology Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero,
Yuseong-gu, Daejeon 34057, Korea*

**Corresponding author: hshim@kaeri.re.kr*

1. Introduction

The world has agreed to use low-carbon energy sources to achieve the Paris Agreement's goal of limiting the rise in global temperature to below 2°C [1]. Thereby, use of renewable energy such as wind and solar power sources have been continuing to grow. Nuclear power is also being considered as a promising energy source to replace fossil fuels for base power [2,3]. Particularly, small modular reactors (SMRs), which have the electric capacity less than 300 MW, have been widely developed by many types of reactors such as water cooled, liquid cooled, gas cooled, and molten salt cooled reactors, in various applications [3,4]. Among them, integrated water-cooled reactors occupies the largest proportion of SMR designs due to long-time operation experiences in light water-cooled reactors (LWRs). The soluble boron-free reactor, which control the excess reactivity of core with only burnable absorber, is also one of the key technologies in water-cooled SMRs [5,6].

Stainless steels are widely used in primary circuits of pressurized water reactor (PWR) due to its high corrosion-resistances. Type 304 and 316 austenitic stainless steels are the main materials used for the structures supporting the nuclear core in the reactor pressure vessel and for pressurized boundary piping of PWR primary circuits. It is expected that these stainless steels will also be used as the main structural element in SMR [7]. However, stainless steels have rarely been tested in a boron-free primary coolant chemistry of SMRs. The alkaline chemistry, including the alkaline pH agents such as NH_3 , KOH , LiOH , and ETA (Ethanalamine), in which the structural materials were thermodynamically more stable, can be considered as a primary coolant chemistry of SMRs [8,9].

Thus, we investigated the corrosion behavior characteristics such as corrosion and release of stainless steel 316L (STS 316L) under high-temperature alkaline solution in this work. The corrosion and release tests were performed at 310°C for 10,000 hours with 6 interrupts using simulated primary chemistry loops. The corrosion, release rates were measured along with analysis of oxide layer for tested specimen.

2. Experiments

STS 316L tube with an outer diameter of 19.05 mm and a wall thickness of 1.2 mm was used in test of its corrosion and release. Corrosion and release test equipment were composed of a 3.75L autoclave and circulating primary coolant system as shown in Fig. 1. A test solution to simulate the boron-free primary coolant of SMR was prepared by adding 100 ppm ammonia into deionized water and its pH was measured as about 10.5 at 25°C. The dissolved oxygen concentration and

dissolved hydrogen concentration of the test solution were adjusted to less than 5 ppb and 35 cc(STP)/kg· H_2O , respectively. The system pressure and temperature in the test autoclave were kept at 150 bar and 310°C, respectively. Then, pH_T of a primary coolant, which is calculated using ChemWorks™ software, was a 6.9 at 310°C. The corrosion and release tests were conducted for totally 10,000 hours with 6 breaks (500, 1000, 2000, 4000, 6000, and 10000h).

The corrosion rate of tested specimens was evaluated by gravimetric analysis based on a chemical descaling method [10]. The corroded specimens were descaled using a two-step alkaline permanganate and ammonium citrate process. The first step was immersed in a mixture aqueous solution of 1% KMnO_4 and 5% NaOH at 90°C for 30 min, followed by wiping with a cloth. The second step was immersed in a 5% ammonium citrate solution at 90°C for 30 min, followed by wiping with a cloth. After both steps, the weight of the specimen was measured using a 5-place balance. In this way, the two-step descaling process was repeated on each specimen six to ten times. To correct the base metal losses due to corrosion during the descaling process, the incremental weight losses were reversely linear-extrapolated, according to the ASTM G1-67. The release rate was evaluated from initial weight, metal weight in oxide layer and descaled metal weight. The morphology, chemical composition and microstructure of the surface oxide layer were investigated using SEM-EDS and X-ray diffraction.

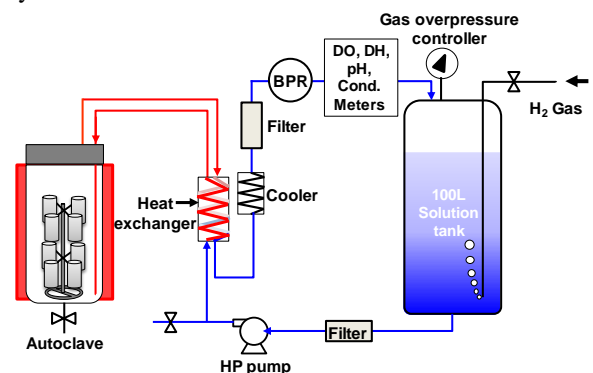


Fig. 1. Schematic of the primary water recirculating system used for the corrosion/release test.

3. Results and discussion

The corrosion and release rates of STS 316L tube were evaluated with increase in test time as shown in Fig.2 and as summarized in Table 1. The corrosion rate of STS 316L in alkaline solution abruptly decreases up to 4000 hours and then converges to a constant value. The release rate also shows a similar trend with the corrosion rate as the test time increases. However, the release/corrosion (RR/CR) ratio is in the range

of 0.26 to 0.32, which is smaller than general value in PWR reported by other research groups [11,12]. In addition, the effect of test time on release/corrosion ratio is negligible, excepting the result of corrosion test for 500 and 1,000 hours. This is probably because STS 316L has higher corrosion resistance in an alkaline primary coolant than in Li-B primary coolant.

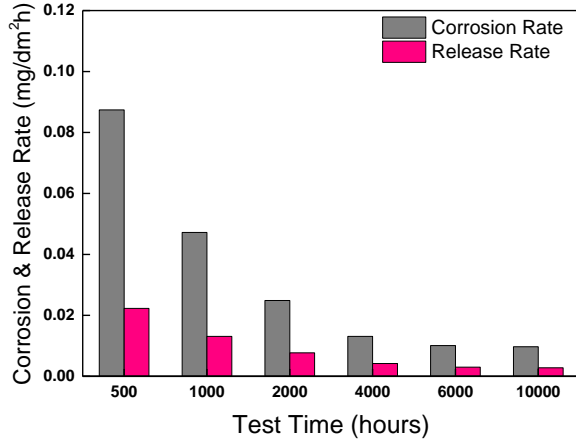


Fig. 2. Corrosion and release rate of STS 316L in alkaline primary coolant with increase in test time.

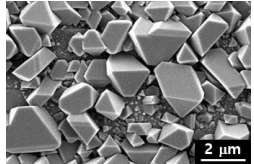
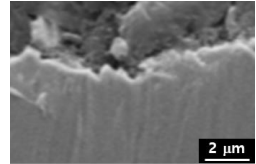
Table 1. Corrosion and release rates, Release/Corrosion ratio of STS316L corroded in alkaline primary coolant.

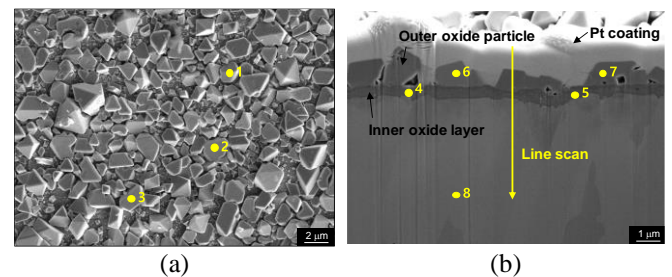
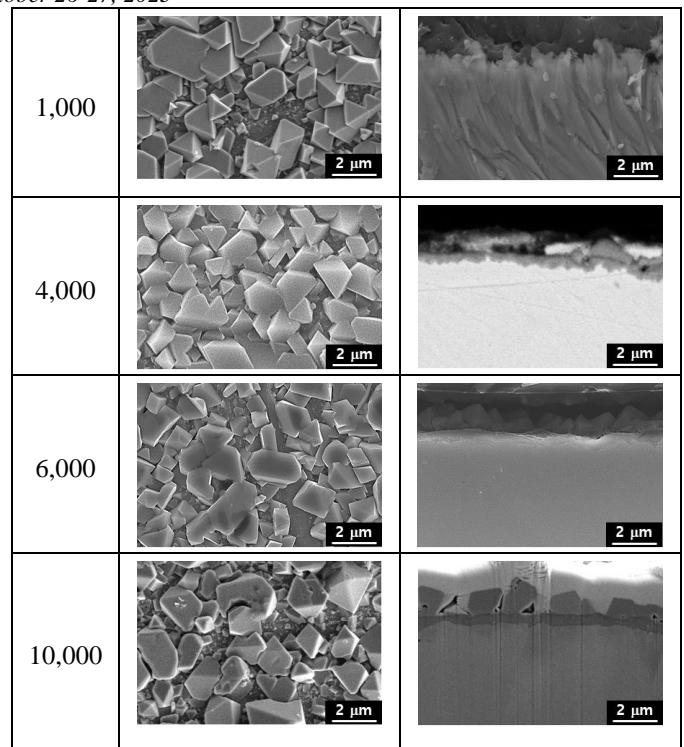
Test time (h)	Corrosion rate (mg/dm ² h)	Release rate (mg/dm ² h)	CR/RR ratio
500	0.0874	0.0223	0.255
1,000	0.0472	0.0131	0.277
2,000	0.0249	0.0077	0.309
4,000	0.0131	0.0042	0.320
6,000	0.0101	0.0030	0.297
10,000	0.0097	0.0028	0.289

Table 2 shows the surface and cross-sectional SEM micrographs of corroded specimens with increase in test time. The polyhedral particles with sub-micron to several micrometer size were observed on the specimen corroded for 500 hours and those gradually grown with increase in test time. In addition, the thickness of oxide layer also gradually grown with increase in test time as summarized in Table 2. In addition, the chemical composition was mainly analyzed by nickel ferrite (NiFe₂O₄) or nickel chromite (NiCrO₃) as shown in Fig. 3. The thickness of oxide layer for specimen tested during 10,000 hours was investigated with about 1 μm as shown in Fig. 3(d) for line scan in Fig. 3(b).

The XRD patterns depict that the oxide layer is composed of nickel ferrite and nickel chromite corresponded with the result of SEM-EDS.

Table 2. Surface and cross-sectional SEM images of STS 316L corroded in alkaline primary coolant.

Time (h)	Surface	Cross-section
500		



Point EDS	Chemical composition (wt%)				
	O	Cr	Fe	Ni	Total
1	21.60	4.03	66.05	8.32	100.00
2	17.51	6.00	68.72	7.77	100.00
3	17.21	4.32	70.80	7.67	100.00
4	5.38	20.97	60.82	12.83	100.00
5	3.85	22.51	60.18	13.46	100.00
6	8.09	10.92	70.72	10.26	100.00
7	7.33	7.76	75.55	9.36	100.00
8	0.40	16.81	72.38	10.40	100.00

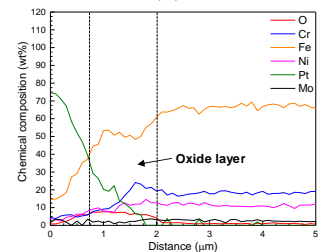


Fig. 3 SEM-EDS analysis result of STS 316L corroded for 10,000 hours in alkaline coolant; (a) Surface SEM image, (b) cross-sectional SEM image, (c) EDS point analysis, and (d) line profile on cross-section.

The change in microstructure of corroded specimens was not observed for increasing test time. The XRD patterns depict that the oxide layer is composed of nickel ferrite and nickel chromite corresponded with the result of SEM-EDS. The change in microstructure of corroded specimens was not observed for increasing test time.

Therefore, it can be understood that the size of oxide particles and thickness of the inner and outer oxide films respectively increase with increase in test time, while there is no change in the chemical composition and microstructure of the oxide films.

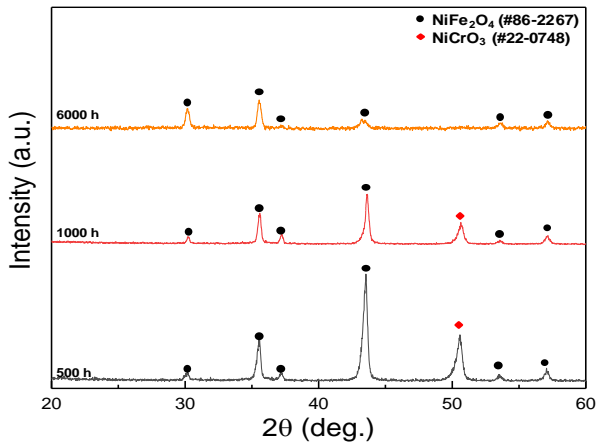


Fig. 4 X-ray diffraction patterns of STS 316L corroded in alkaline solution with increase in test time.

4. Conclusions

In this work, we investigated the corrosion and release rates along with analyzing characteristics of oxide layer of STS 316L tested at 310°C for 10,000 hours in the simulated primary water containing alkaline agent. The corrosion rate was measured by 0.0874 mg/dm²h in the specimen tested for 500 hours and it decreased abruptly in early stage and converged to the constant value with increase in test time. The size of outer oxides and the thickness of oxide layer were gradually increased with increase in test time. In addition, the release rate of STS 316L in alkaline solution shows the 0.26 to 0.32 times of corrosion rate and it is slightly lower value compared to the results in Li-B PWR chemistry condition. However, the chemical composition of oxide layer was similar with that formed STS 316L tested in Li-B PWR water chemistry. Therefore, it is predicted that such results will be an important data for chemistry design of SMRs.

Acknowledgments

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