

Corrosion Behavior of Borated Stainless Steel in High DO-Borated Water Environment

Daehyeon Park ^{a*}, Yunju Lee ^a, Junhyuk Ham ^a, Seung Chang Yoo ^a, Kiyoung Kim ^b, Donghee Lee ^b and Ji Hyun Kim ^{a†}

^a Department of Nuclear Engineering, Ulsan National Institute of Science and Technology (UNIST), 50, UNIST-gil, Ulsan 44919, Republic of Korea

^b Korea Hydro & Nuclear Power Corporation, 70, Yuseoung-daero 1312, Yuseong-gu, Daejeon 34101, Republic of Korea

*Corresponding author: kimjh@unist.ac.kr

1. Introduction

Used nuclear fuels are stored in spent fuel pool (SFP) until radioactivity of the fuel decreased sufficiently to be stored in canister. Since it is difficult to repair or replace SFP storage rack, the material used for storage rack should maintain high corrosion resistance and neutron absorbency. In Korea, borated stainless steel (BSS), stainless steel contains certain amount of boron is used as SFP storage rack material. Due to low solubility of boron in austenitic stainless steel, boron was added in the form of metallic borides, (Fe, Cr)₂B.

BSS is known to suffer pitting corrosion and galvanic corrosion between substrate and secondary phases [2]. Previous study also reported that Cr content difference between metallic borides and substrate affects the short-term oxidation behavior of BSS [1]. However, corrosion behavior of BSS in SFP condition which contains high dissolved oxygen (DO) concentration and high boron concentration, is not fully understood. Also, long-term corrosion study was not conducted for this material [3,4].

Therefore, to understand long-term corrosion and oxidation behavior of BSS, accelerated corrosion experiment was conducted in simulated SFP condition. Detail microstructural analysis was conducted with scanning electron microscope (SEM) attached focused ion beam (FIB) and energy dispersive X-ray spectroscopy (EDS).

2. Experiments

2.1 Accelerated corrosion experiments condition

In general, SFP is large enough to containing several tens of hundreds of used fuels. Therefore, water chemistry and temperature in SFP is dependent on its position. In average, water environment of SFP is known to contains 4200 ppm of boron and about 25.3 °C. DO concentration is generally not monitored, however, since

it is open air condition it could be assumed as saturated condition, which is 8000 ppb in room temperature.

Accelerated corrosion experiment was designed based on the oxidation characteristics of SS304, because oxidation of BSS is not revealed, yet. From previous study, oxidation mechanism of SS304 were maintained as same below 250 °C and the corrosion rate was proportional to temperature. The oxide layer growth activation energy of SS304 was calculated to 21.3 kJ/mol [5]. And it was assumed that oxidation of BSS is governed by Arrhenius equation. Thus, to simulate 0.5, 5, 10 years of corrosion in SFP environment, specimens were exposed to accelerated condition for 0.2, 2 and 4 months, respectively.

2.2 Sample preparation.

The chemical composition of specimen used in this study is presented in Table I. The specimen was fabricated with electrical discharge machining to 20 mm × 20 mm × 3 mm with a 2 mm of hole on one side which was used to hanging the specimen in autoclave with Pt wire insulated with zirconia sleeve. All specimens were grounded up to 800 grit before experiments.

2.3 Analysis method

Specimens were taken out from autoclave for each 0.2, 2 and 4 months. Then those were rinsed carefully with deionized water. To investigate the microstructural characteristics of specimen, the ex-situ investigation was conducted using SEM coincidence with EDS. To observe the cross section of specimens, FIB milling method was also used.

Table I. Chemical composition of BSS specimen

Fe	Cr	Ni	C	Mn	P	S	Si	N	B
Bal	18.0~20.0	12.0~15.0	0.08	2.00	0.045	0.03	0.75	0.1	1.8

3. Results and Discussion

3.1 As-received specimen

Figure 1 (a) shows secondary electron image of surface of as-received specimen. Two phases of substrate and metallic borides were observed throughout the specimen. Since boride has higher hardness than substrate, substrate was grounded more than boride. Red arrow indicates the area where line EDS analysis was conducted which is presented in figure 1 (b).

Secondary phase is found to be metallic boride, $(FeCr)_2B$, which is assumed to be formed during production process because of the low solubility of boron in austenitic stainless steel. The composition of substrate was similar to SS304, however, it has lower Cr content and higher Ni contents than SS304.

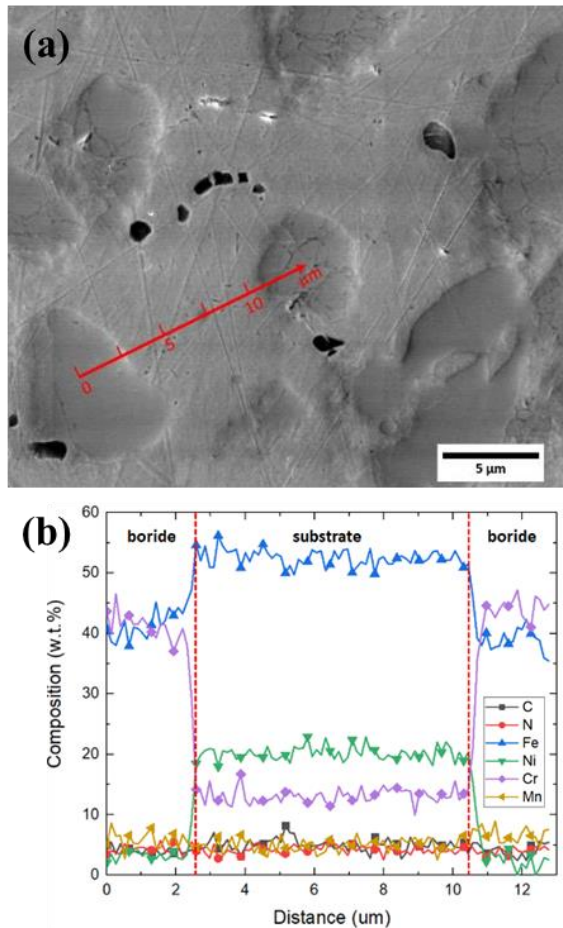


Fig. 1. (a) Secondary electron image of surface of specimen and (b) line EDS results of As-received specimen

3.2 Surface morphology of oxidized BSS specimen

Figure 2 shows secondary electron image of oxidized specimens. As the exposure time increased, pitting corrosion and oxide film was developed on overall

surface of BSS. BSS known to undergoes pitting corrosion in corrosive environment, and it was observed also in this study as marked with red circle in figure 2, mostly on substrate surface. Pitting corrosion was numerous observed in specimen which was exposed shorter time. However, the number of it was reduced with increased exposure time due to growth of oxide film on the surface.

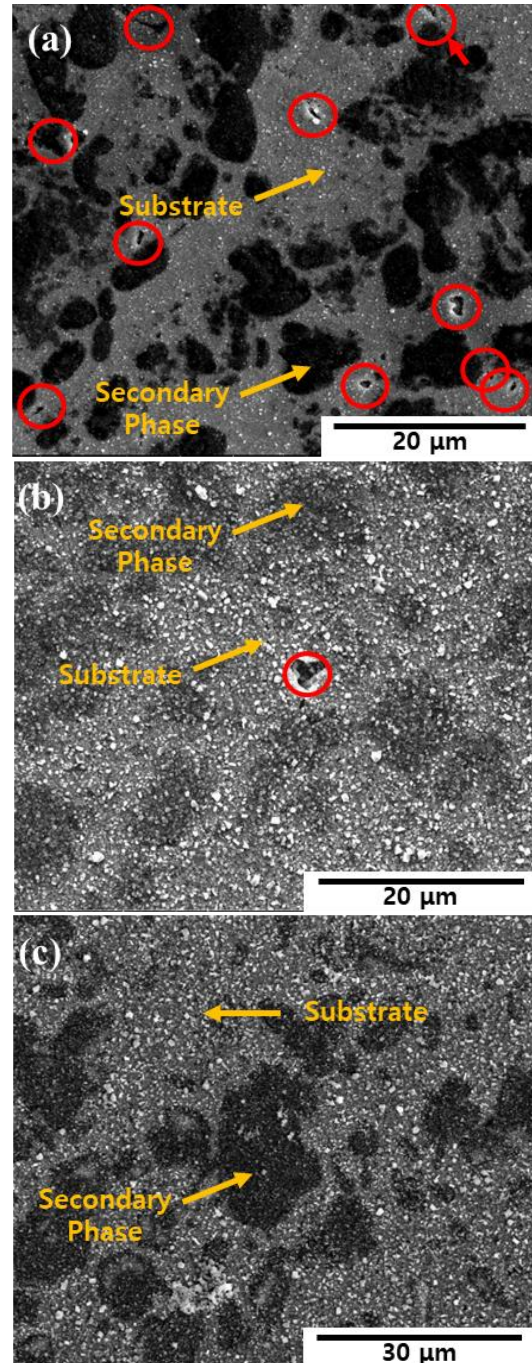


Fig. 2. Secondary electron images of specimen surface after (a) 0.2 months, (b) 2 months and (c) 4 months of accelerated corrosion experiment. Red circle indicates pitting corrosion observed.

3.3 Cross section of BSS specimen after the experiments

Figure 3 shows SEM images of cross section of specimens after accelerated corrosion experiment. Those images were taken at the place where pitting corrosion observed. As shown in the figures, after pitting corrosion occurs in early stage of oxidation, the oxide film grew. Also, the secondary phase which was exposed to water was oxidized. Figure 4 shows thickness of oxide observed after accelerated corrosion experiment. Thickness of oxide film was depending on the exposure time. It can be observed that the thickness of the oxide film increases as the exposure time increases.

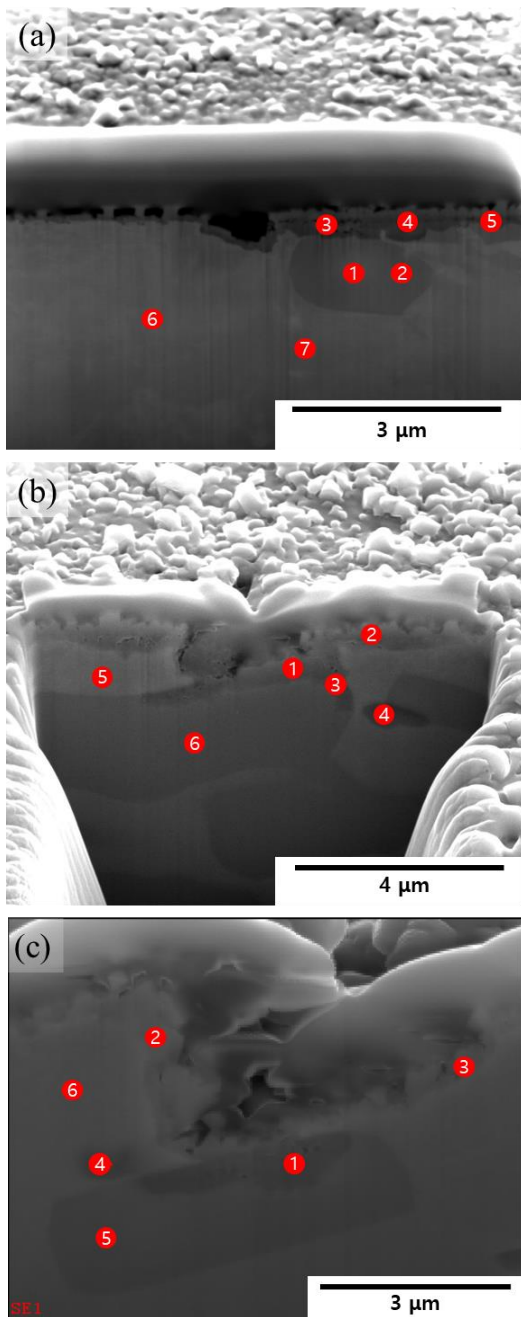


Fig. 3. SEM images of cross section of specimens after (a) 0.2 months, (b) 2 months and (c) 4 months of accelerated corrosion experiment. Red circle indicates where EDS point analysis was conducted.

Table II: Point EDS results of 0.2 months exposed specimen presented in figure 3 (a)

Type (a.t.%)	O	Cr	Fe	Ni
1	6.04	53.5	36.4	2.2
2	5.65	51.38	38.2	2.65
3	17.28	24.78	43.11	7.26
4	18.34	18.53	44.8	9.27
5	18.3	22.07	41.66	7.17
6	3.11	14.86	71.29	8.06
7	2.96	15.31	71.21	7.89

Table III: Point EDS results of 2 months exposed specimen presented in figure 3 (b)

Type (a.t.%)	O	Cr	Fe	Ni
1	27.62	33.95	24.87	8.45
2	28.53	12.21	17.94	17.92
3	23.08	41.0	30.1	1.76
4	21.7	55.23	17.5	3.93
5	7.13	23.66	50.99	12.49
6	8.84	58.3	27.63	2.7

Table IV: Point EDS results of 4 months exposed specimen presented in figure 3 (c)

Type (a.t.%)	O	Cr	Fe
1	18.94	27.21	50.92
2	19.64	13.45	50.43
3	11.25	7.79	25.07
4	14.91	18.22	63.87
5	5.2	54.46	39.44
6	3.19	15.74	78.89

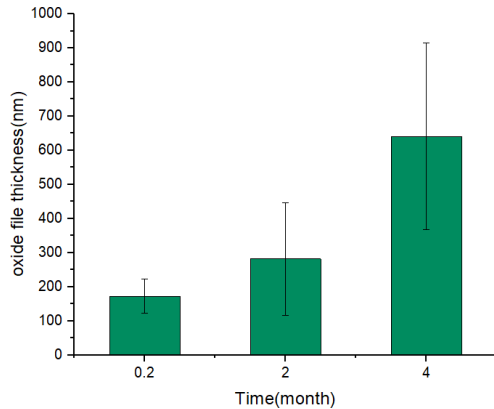


Fig. 4. Oxide film thickness of BSS specimens after accelerated corrosion experiment.

Figure 5 shows cross section of specimen after 4 months of accelerated corrosion experiment. As shown in the figure, secondary phase exposed to water was oxidized. From EDS analysis result shown in figure 5 and table V, darker area observed in figure 5 is oxidized particle which have higher oxygen concentration. And Cr contents were decreased compared to the non-oxidized secondary phase. Oxidized particle observed in 4 months of accelerated corrosion experiment shows porous oxide media. The secondary phase particles in 0.2 and 2 months exposed specimen also have porous oxide which contains relatively lower chromium elements and higher oxygen elements.

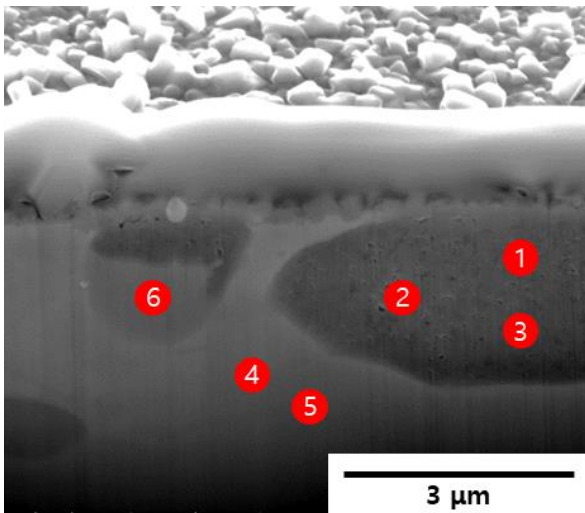


Fig. 5. SEM image of cross section of specimen after 4 months of accelerated corrosion experiment. Red circle indicates where EDS point analysis was conducted.

Table V: Point EDS results of 4 months exposed specimen presented in figure 4.

Type(a.t.%)	O	Cr	Fe	Ni	
Oxidized secondary phase	1	30.04	8.35	59.61	2.00
	2	29.85	9.58	58.5	2.07
	3	29.09	8.36	60.1	2.45

Substrate	4	4.12	15.89	71.94	8.05
	5	3.95	8.09	73.68	8.09
Secondary phase	6	18.01	26.97	52.00	3.01

4. Conclusions

To investigate the long-term corrosion behavior of BSS in SFP environment, accelerated corrosion experiments were conducted for 0.2, 2 and 4 months to simulate 0.5, 5 and 10 years. Pitting corrosion was observed during early stage of corrosion experiment. And oxide growth was observed on the surface of specimen and its depth grew as time goes by. Although the oxide thickness was increased by increased exposure time, 4 months exposed specimen, which simulated 10 years in SPFs, did not exceed 1 μm . Also, secondary phase exposed to water were oxidized and show porous oxide media.

ACKNOWLEDGEMENT

This work was financially supported by Korea Hydro & Nuclear Power Co., Ltd.

REFERENCES

- [1] Moreno, D.A.; Molina, B.; Ranninger, C.; Montero, F.; Izquierdo, J. Microstructural Characterization and Pitting Corrosion Behavior of UNS S30466 Borated Stainless Steel. *Corrosion* 2004, 60, 573–583
- [2] Lister, T.E.; Mizia, R.E.; Erickson, A.W.; Matteson, B.S. General and Localized Corrosion of Borated Stainless Steels; INL/CON-07-135355; Idaho National Laboratory: Idaho Falls, ID, USA, 2008.
- [3] Robertson, J. "The Mechanism of High Temperature Aqueous Corrosion of Steel." *Corrosion Science* 29, no. 11-12 (1989): 1275-91.
- [4] Ha, Heon Young, Jae Hoon Jang, Tae Ho Lee, Chihyoung Won, Chang Hoon Lee, Joonoh Moon, and Chang Geun Lee. "Investigation of the Localized Corrosion and Passive Behavior of Type 304 Stainless Steels with 0.2-1.8 Wt % B." *Materials* 11, no. 11 (2018): 1–15.
- [5] Duan, Zhengang, Farzin Arjmand, Lefu Zhang, and Hiroaki Abe. "Investigation of the Corrosion Behavior of 304L and 316L Stainless Steels at High-Temperature Borated and Lithiated Water." *Journal of Nuclear Science and Technology* 53, no. 9 (2016): 1435–46.
- [6] Kuang, W., Wu, X., & Han, E. H. (2012). Influence of dissolved oxygen concentration on the oxide film formed on 304 stainless steel in high temperature water. *Corrosion Science*, 63, 259–266.
<https://doi.org/10.1016/j.corsci.2012.06.007>