

Corrosion Behavior of (Fe,Cr)₂B Metallic Boride of Borated Stainless Steel in Borated Water Environment

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1. Introduction

In many nuclear power plant sites in Korea, high density storage racks were installed in the spent fuel pool (SFP) to expand the spent fuel storage capacity. To maintain nuclear criticality of spent fuels borated stainless steel (BSS), stainless steel contains certain amount of boron is used as SFP storage rack material. Since it is difficult to repair or replace SFP storage rack, the material used for storage rack should maintain high corrosion resistance.

BSS is known to suffer pitting corrosion and galvanic corrosion between substrate and secondary phases [1-3]. Previous study also reported that Cr content difference between metallic borides and substrate affects the short-term oxidation behavior of BSS [4]. 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, 5-7].

Therefore, to understand long-term corrosion behavior of BSS, accelerated corrosion experiment was conducted in simulated SFP condition.

2. Experiments

2.1 Accelerated corrosion experiments condition

The spent fuels are cooled by 4200 ppm and 25.3 °C of boric acid in SFP. Because it is open air condition, DO concentration of the pools assumed to be 2000 ppb based on the previous research which confirmed that oxidation behavior of stainless steel is maintained over 300 ppb [5].

Corrosion mechanisms are transformed if system temperature increased over certain value. From previous

studies, corrosion of SS304 can be occurred below 250 °C and the corrosion activation energy of SS304 is proportional to temperature and inversely proportional to DO concentration in boric acid. The corrosion activation energy of SS304 in 2000 ppb of DO and 250 °C of boric acid is calculated to be 21.3 kJ/mol [6]. Acceleration coefficient in this condition was 30 according to Arrhenius equation.

Thus, to simulate the 0.5, 5, 10, 15 and 20 years of corrosion in SFP, BSS specimen were exposed to 250 °C, 2000 ppb of DO, 4200 ppm of boric acid for 0.2, 2, 4, 6 and 8 months. This paper covers detailed investigation about oxidation behavior of the 8 months exposed specimen.

2.2 Sample preparation

The chemical composition of specimen used in this study is presented in Table 1. The specimen was fabricated with electrical discharge machining to 20 mm × 20 mm × 3 mm with a 2 mm 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

To investigate the microstructural characteristics of specimen, the ex-situ investigation was conducted using Scanning Electron Microscope (SEM) coincidence with Energy Dispersive X-ray Spectroscopy (EDS). To observe the cross section of specimens, Focused Ion Beam (FIB) was also used. Detailed chemical analysis was performed with Electron Probe X-ray Micro-Analyzer (EPMA).

Table 1 Chemical composition of BSS in at. %.

Fe	Cr	Ni	C	Mn	P	S	Si	B
Bal	19.13	12.52	0.08	1.14	0.016	0.0003	0.3	1.88

3.Results and Discussion

3.1 Surface morphology of oxidized specimen

Detailed results and discussion of as-received and earlier specimen were presented in previous study [4]. In summary, microstructure of BSS was composed of substrate and secondary phase, which was $(\text{Fe, Cr})_2\text{B}$. Pitting corrosion was observed in early stage of corrosion. And oxide growth was observed on the surface of specimen and its depth grew as time goes by.

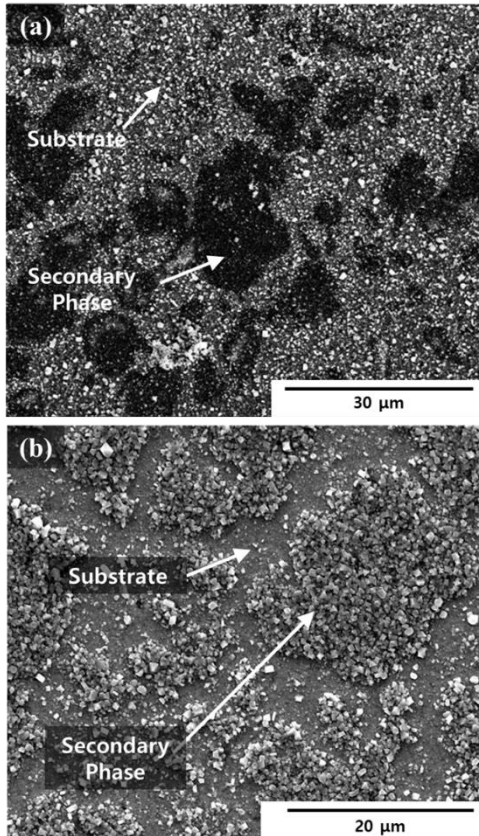


Figure 1 Surface SEM images of BSS specimens after (a) 4 months and (b) 8 months of accelerated corrosion in high DO borated water

Figure 1 shows secondary electron image of oxidized specimens, (a) is earlier specimen which was exposed for 4 months and (b) is the specimen exposed for 8 months. Oxides formed on the specimen exposed for 8 months are larger than those of specimen exposed shorter time. Besides, oxides were densely packed on the secondary phase particle than substrate.

3.2 Cross section of oxidized specimen

Figure 2 shows SEM images of cross section of specimens after accelerated corrosion experiment. As shown in the figure, oxide layer formed on substrate is thinner than that on the secondary phase. As shown in Figure 3, thickness of oxide layer forms on secondary

phase increases dramatically after exposed for 6 months.

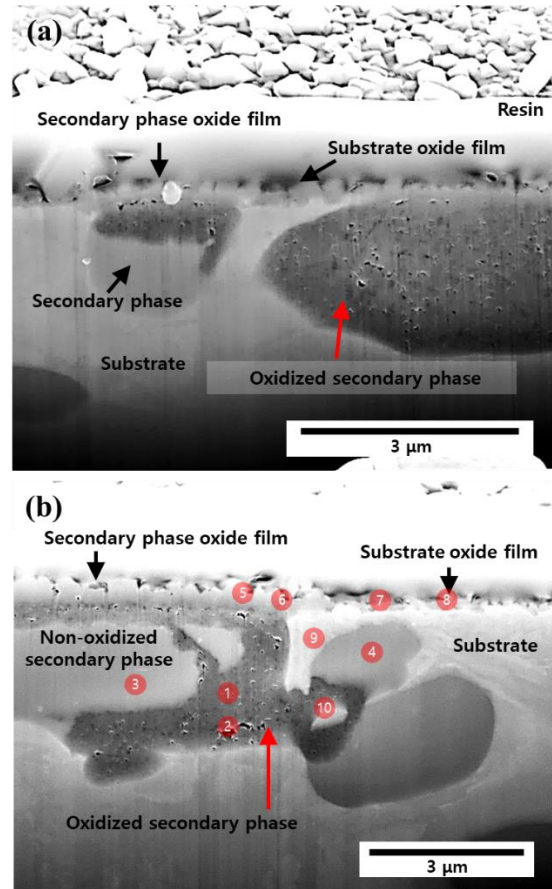


Figure 2 Cross section SEM images of BSS specimens after (a) 4 months and (b) 8 months of accelerated corrosion in high DO borated water. EDS points were indicated in each image.

Table 2 Point EDS results of 8 months exposed specimen presented in figure 2 (b)

Type		O (at.%)	Cr (at.%)	Fe (at.%)	Ni (at.%)
Oxidized secondary phase	1	26.18	14.1	56.28	3.44
	2	23.13	15.02	56.47	5.38
Non-oxidized secondary phase	3	7.64	54.8	36.03	1.53
	4	6.43	55.23	36.64	1.7
Oxide film of secondary phase	5	27.91	17.85	36.55	17.68
	6	25.73	15.92	41.57	16.78
Oxide film of substrate	7	7.24	18.86	55.45	18.46
	8	4.34	24.64	54.49	16.53
Substrate	9	5.86	22.84	60.05	11.25
	10	10.95	24.02	56.97	8.05

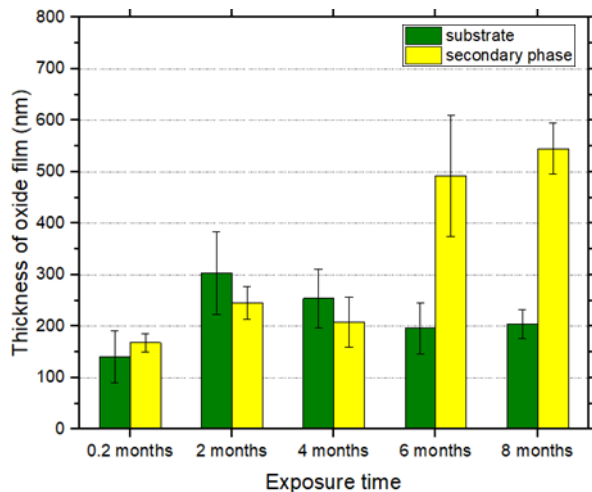


Figure 3 Oxide thickness change of substrate and secondary phase in BSS specimen.

Also, secondary phases which were exposed to water were oxidized as shown in red arrow of Figure 2. Oxidized secondary phase have porous structure and contains higher Fe and lower Cr contents than non-oxidized secondary phase. (Table 2)

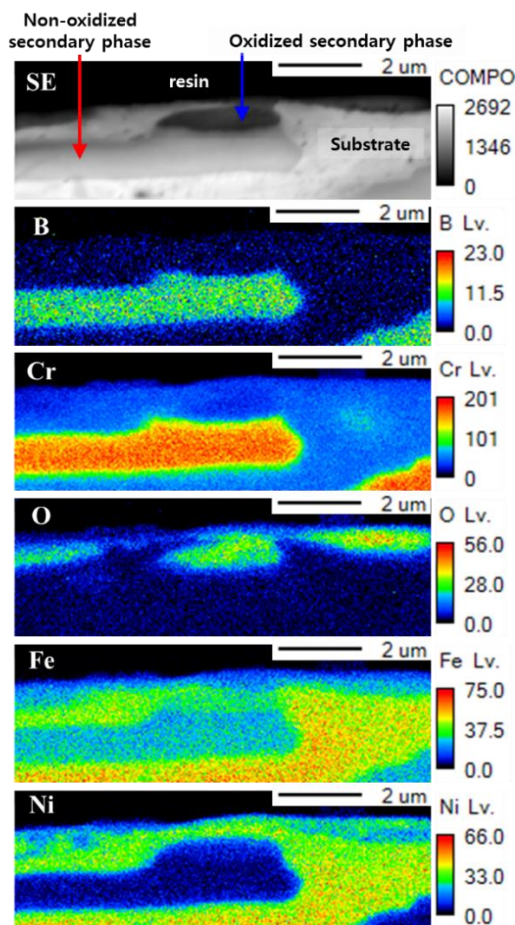


Figure 4 Cross section EPMA mapping images of BSS specimens after 8 months of accelerated corrosion in high DO borated water

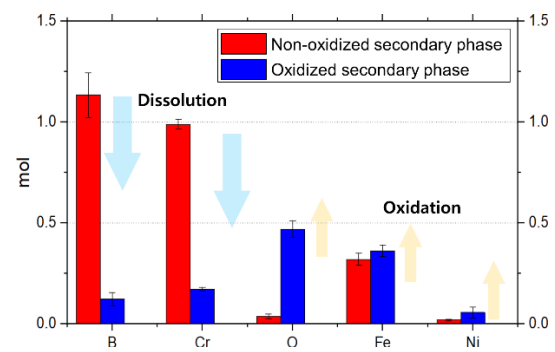


Figure 5 Quantitated EPMA analysis results of oxidized and non-oxidized secondary phase in Figure 4

EPMA mapping image (Figure 4) and its quantitated data (Figure 5) show changes of chemical composition between non-oxidized and oxidized secondary phase. The results indicate that B and Cr are dissolved from secondary phase during oxidation and leave porous oxidized media. Whereas Fe and Ni contents of oxidized secondary phase are slightly increased.

It could be thought that oxidized secondary phase which have porous structure could give better diffusion path than non-oxidized phase and cause thicker and denser oxide layer in specimen oxidized for 6 months or longer.

4. Conclusions

To investigate the long-term corrosion behavior of BSS in SFP environment, accelerated corrosion experiments were conducted for 0.2, 2, 4, 6 and 8 months to simulate 0.5, 5, 10, 15 and 20 years.

Thickness of oxide layer forms on secondary phase increases faster than substrate and it is prominently featured after exposed for 6 months. It could be thought that during oxidation of secondary phase, B and Cr are dissolved leaving porous oxidized media which could give better diffusion path than non-oxidized phase.

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