Long-term Oxidation Behavior of Borated Stainless Steel in Spent Fuel Pool Environment

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1. Introduction

In several spent fuel pool (SFP), borated stainless steel (BSS) is used as structural material of spent fuel pool high density storage rack to maintain criticality of spent fuels. Because it is difficult to replace storage rack, corrosion resistance and neutron absorbency are required for long period.

BSS is based on stainless steel 304 and it is specified in the ASTM A887-89 standard depending on the boron concentration form 304B (0.20-0.29% B) to 304B7 (1.75-2.25% B) [1]. Because of low solubility of boron in austenitic stainless steel, metallic borides such as (Fe, Cr)$_2$B are formed as secondary phase. Previous study reported that Cr content difference between metallic borides and substrate affects the short-term oxidation behavior of BSS [2,4]. 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. Due to these reasons, 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

To simulate long-term corrosion of BSS, experiment at accelerated temperature was planned since it is not possible to conduct corrosion test for several decades.

Operating environment of SPF is 25 ℃ with 4,200 ppm of boron ion and atmospheric air condition. Even though it's atmospheric air condition, DO concentration which affects corrosion rate of BSS is not measured during operation. In this experiment, it was assumed to be 2,000 ppb according to previous study which reports that oxidation behavior of stainless steel is maintained over 300 ppb [3].

Corrosion mechanisms are transformed if system temperature increased over certain value. From previous studies, corrosion of SS304 can be occurred equally below 250 ℃ 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 2,000 ppb of DO

and 250 ℃ of boric acid is calculated to be 21.3 kJ/mol [4]. As explained above studied, accelerated coefficient was 30 times according to Arrhenius equation.

Thus, to simulate the 0.5, 5, 10, 15, 20 and 30 years of corrosion in SFP, BSS specimen were exposed to 250 ℃, 2,000 ppb of DO concentration, boric acid with 4,200 ppm of boron ion for 0.2, 2, 4, 6, 8 and 12 months.

2.2 Sample preparation

The chemical composition of specimen used in this study is presented in Table 1. The specimen was cut into 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 polished with SiC paper up to 800 grits, then ultrasonically cleaned in deionized water.

Table I: Chemical composition of BSS [wt.%]

Fe	B	Cr	Ni	C
Bal	2.07	20.28	13.32	0.08
Mn	Si	P	S	
1.30	0.29	0.01	0.0003	

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 spectroscope (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).

3. Results and Discussions

3.1 Morphology of oxidized specimen

Detailed results and discussion of as-received and earlier specimen were presented in previous study [5]. In summary, microstructure of BSS was composed of substrate and secondary phase, which was (Fe, Cr)$_2$B.
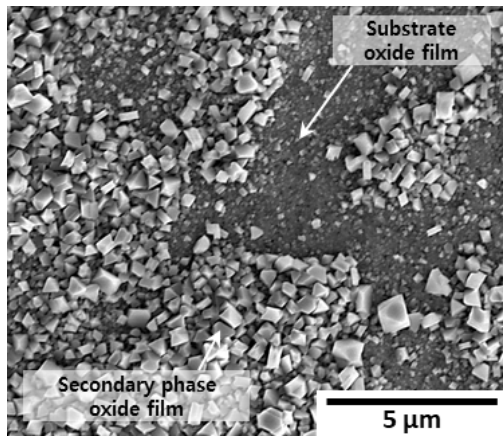
Figure 1 Surface SEM images of BSS specimens after 12 months of accelerated corrosion in high DO borated water

Figure 1 shows secondary electron image of oxidized specimens exposed for 12 months. Oxide film formed on BSS was grown in a polyhedral form on surface of both substrate and secondary phase. Especially, oxide on secondary phase grow larger than substrate it. Besides, oxides were densely packed on the secondary phase particle than substrate.
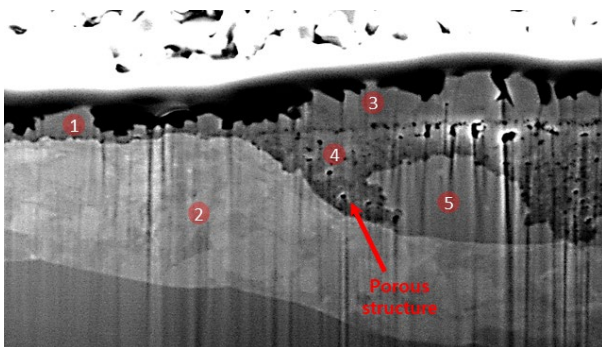

Figure 2 Cross section SEM images of BSS specimens after 12 months of accelerated corrosion in high DO borated water. EDS points were indicated in each image

Table Ⅱ: Point EDS results of 12 months exposed specimen presented in figure 2

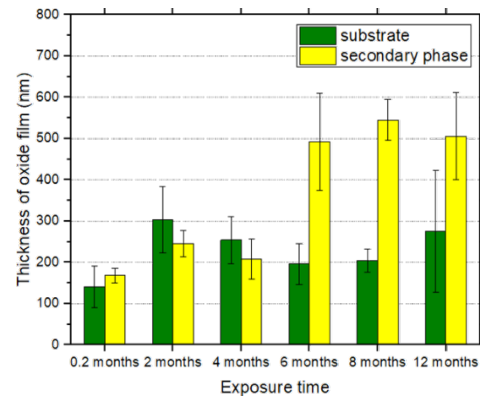| Type		O (at.%)	Fe (at.%)	Cr (at.%)	Ni (at.%)
Oxide film of substrate	1	32.84	27.49	11.64	28.03
Substrate	2	8.11	53.52	25.69	12.68
Oxide film of secondary phase	3	40.51	21.79	12.86	24.85
Oxidized secondary phase	4	43.24	28.48	18.68	9.61
Secondary phase	5	8.02	25.57	63.63	2.79

Figure 2 Oxide thickness change of substrate and secondary phase in BSS specimen

Figure 2 shows SEM images of cross section of specimens after accelerated corrosion experiment for 12 months. As shown in the figure, oxide layer formed on substrate is thinner than that on the secondary phase. Also, secondary phases which were exposed to water were oxidized as shown in red arrow of Figure 2. Oxidized secondary phase have porous structure.

Oxide film formed on the substrate and secondary phase is considered to Fe_2O_3, $NiFe_2O_4$, and Cr_2O_3 from EDS analysis, which are passivation layers formed in a high DO concentration environment of general stainless steel.

As shown in Figure 3, the clearly difference in oxide film thickness between substrate and secondary phase after 6 months could indicate that secondary phase is oxidized more.
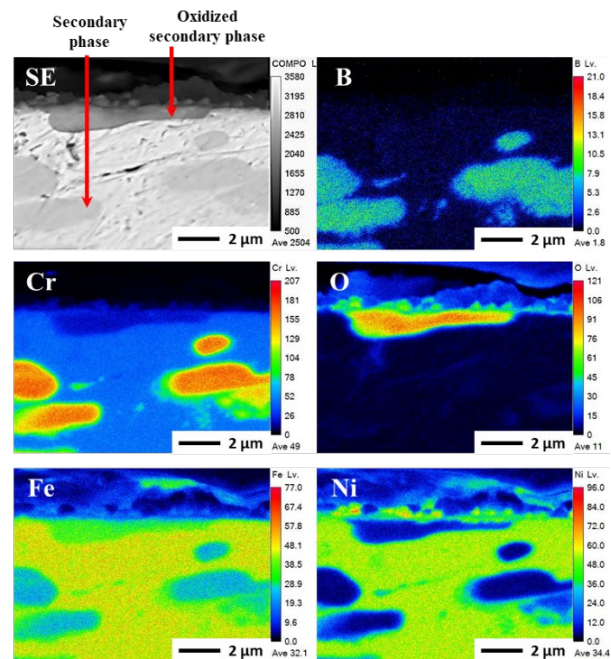

Figure 3 Cross section EPMA mapping images of BSS specimens after 12 months of accelerated corrosion in high DO borated water

Figure 4 shows EPMA analysis results of cross section of specimens after 12 months for accelerated corrosion experiment. As shown in the figure, the chemical composition of Fe, Cr, Ni, B and O were analyzed. B and Cr in oxidized secondary phase seems to significantly reduce compared to that of non-oxidized secondary phase. It could be thought that oxidation of B and Cr had the lowest Gibbs free energy compared to other elements. Due to oxidized B has high solubility in water, it was dissolute outside and Cr formed unstable oxidation state. Thus, the secondary phase is oxidized into a porous structure, leading to an increase in diffusion rate of metal elements in the surrounding substrate.

4. Conclusions

To investigate the long-term corrosion behavior of BSS which is used as structural material in SFP, an accelerated corrosion experiment and following analysis were carried out. Accelerated corrosion experiments were conducted for 0.2, 2, 4, 6, 8 and 12 months to simulate 0.5, 5, 10, 15, 20 and 30 years.

Thickness of oxide layer forms on secondary phase increases faster than substrate and it is prominently featured after exposed for 6 months. Secondary phase also more oxidized than substrate.

From Gibbs free energy of each oxidation reaction, oxidation of B has the lowest Gibbs free energy compared to other elements. Oxidized B which has characteristic of soluble in water, oxidized secondary phase has porous structure. In this situation, it works as diffusion path for metal elements in the surrounding substrate. It is determined that an oxide film of secondary phase is thicker than substrate oxide film was formed in the secondary phase due to an increased diffusion rate.

In the future, electrochemical properties will be measured with oxidized BSS in SFP condition. It could be evaluated corrosion resistance in long-term corrosion behavior of BSS.

ACKNOWLEDGEMENT

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