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Study on Accelerated Corrosion Experiment of Al6061-B_4C Neutron Absorbers Considering the Spent Nuclear Fuel Wet Storage Environment

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1. Introduction

Due to the global shortage of spent nuclear fuel storage space, Korea has adopted wet storage by installing high-density racks in spent fuel pools to increase storage capacity. Neutron-absorbing materials are used as structural materials to control the reactivity of densely stored spent nuclear fuel. These neutron absorbers must exhibit excellent thermal neutron absorption capabilities, as well as resistance to corrosion and damage caused by neutron irradiation. Currently, commercially available neutron-absorbing materials include aluminum alloys and stainless steel-based materials, both of which incorporate boron to enhance thermal neutron absorption performance.

Since neutron absorbers must remain in service for several decades in nuclear power plants, performance and integrity evaluations are necessary. To this end, surveillance specimens are installed for periodic assessments. However, corrosion phenomena such as pitting corrosion have been observed in stored surveillance specimens, leading to concerns about the degradation of neutron absorption capability[1]. The discovery of such corrosion in neutron absorbers used for approximately eight years has highlighted the need for further research into the long-term integrity of these materials.

Neutron absorbers installed in high-density racks within wet storage pools are stored for decades and must be replaced if their absorption performance falls below a certain threshold. The replacement of neutron absorbers may pose safety concerns and economic losses. Therefore, integrity evaluations must be conducted to ensure their long-term usability. Due to the long-term degradation characteristics of neutron-absorbing materials used for several decades, evaluating them in actual environments presents significant limitations. Therefore, an accelerated corrosion experiment method was adopted to study the long-term degradation characteristics of Al-B_4C neutron absorbers.

2. Experimental procedure

2.1 Accelerated corrosion experiments condition

To simulate the long-term corrosion of Al-B_4C, an experiment at an accelerated temperature was planned since it is not possible to conduct a corrosion experiment for several decades. The operating environment of the SPF is 25°C with 4,200 ppm of boron ions and atmospheric air conditions. Even though it is an atmospheric air condition, the DO concentration, which affects the corrosion rate of BSS, is not measured during operation. In this experiment, the oxygen saturation concentration was maintained in consideration of the oxygen saturation concentration in the atmosphere, which is 7 to 8 ppm.

The general corrosion behavior of aluminum is well known for its high reactivity, which leads to the immediate formation of an amorphous Al_2O_3 oxide layer upon exposure to a corrosive environment. In aqueous chemical environments within the pH range where the passive Al_2O_3 film remains stable, this oxide layer enhances the corrosion resistance of aluminum.

To evaluate the long-term integrity of neutron-absorbing materials in terms of corrosion, the corrosion reactions occurring in actual environments must be consistent with those observed in simulated environments. According to previous studies, the aluminum oxide layer typically exists as bayerite ($Al_2O_3 \cdot 3H_2O$) and boehmite ($Al_2O_3 \cdot H_2O$) in aqueous chemical environments below 100°C. Under prolonged exposure to aqueous conditions, bayerite is the dominant phase, whereas at temperatures above 100°C, the oxide transforms into the crystalline form of boehmite. Furthermore, as shown in the table below, previous research on the corrosion behavior of aluminum alloys indicates that corrosion behavior in actual wet storage pools remains relatively stable up to approximately 100°C as shown in the table I below. In this experiment, the experiment was conducted at 90 °C. When accelerated to 90°C, the acceleration multiple was derived to derive the maximum simulated time compared to the experimental time. The maximum simulated time varies depending on the experimental time, but it was confirmed that 3 to 21.6 times of acceleration was possible.

Table I: Corrosion Behavior of Aluminum Alloy with Temperature[2,3,4]

	60℃~100℃	**100℃~150 ℃**	**150℃~**
phase transtion	-	-	phase transtion
corrosion behavior	general corrosion pitting corrosion	general corrosion	general corrosion, intercrystal corrosion

2.2 Material preparation

B_4C powder was added to Al melted at 700°C and mixed at a constant rotation speed to ensure uniform distribution of B_4C particles. The casting material was homogenized using HIP (hot isostatic pressing) to remove pores. The chemical composition of Al6061/B_4C, with a B_4C content of 18%, is shown in Table II.

Table II: Chemical composition (wt.%) of 18% B_4C/6061Al

18% B_4C/6061Al					
Si	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**
0.65	0.7	0.25	0.15	0.9	0.07
Zn	**Ti**	**Al**	+	**B**	**C**
0.25	0.15	Bal.		82.13	17.87

The microstructure of the Al-B_4C specimens was analyzed using both an optical microscope (OM) and a Scanning Electron Microscope (SEM) equipped with a Focused Ion Beam (FIB) instrument. Additionally, the chemical composition of the specimens was investigated via Energy Dispersive Spectroscopy (EDS).

2. Results

3.1 Microstructure analysis

The figure II below shows the surface photo of Al6061+18% B_4C in an as-received state and the result of EDS analysis aimed at applying the wet storage tank environment of the specimen as shown in the table III below. As a result of the surface EDS analysis, it can be seen that B_4C particles are uniformly distributed in the Al matrix on the surface.

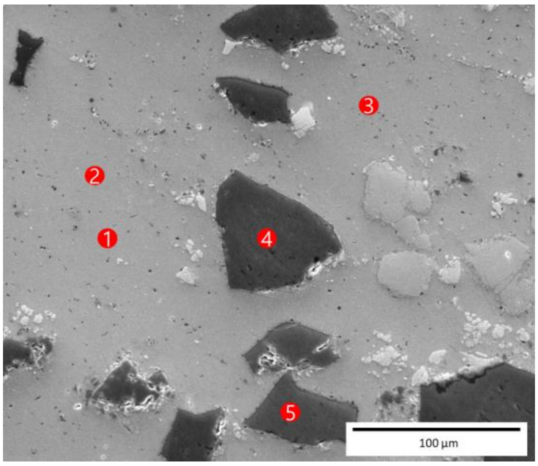

Fig. 2. Al6061+18% B_4C neutron absorber surface image.

Table III: Chemical composition (wt.%) of 18% B_4C/6061Al

Type(a.t.%)		Al	B	C	Mg
Al matrix	1	100	0	0	0
	2	100	0	0	0
	3	100	0	0	0
B_4C	4	0	82.95	16.99	0.06
	5	0	82.24	17.72	0.04

In order to study the surface microstructure of the specimen that underwent an 8 month accelerated corrosion experiment, the analysis was performed using SEM as shown in Fig 3. An aluminum oxide layer was generally formed on the Al matrix. As previously mentioned, the aluminum oxide layer formed in an amorphous state by reacting with hydroxyl (OH) groups in the aqueous environment. To analyze the thickness of the amorphous oxide layer, the cross-section of the oxide layer was examined using a Focused Ion Beam (FIB), revealing an average thickness of approximately 2.1 μm.

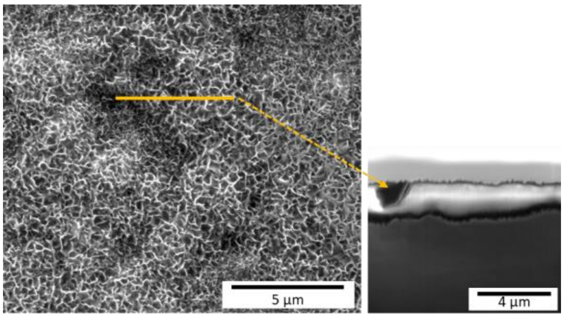

Fig. 3. microstructure images of specimens subjected to corrosion acceleration experiments for 8 months.

While the aluminum matrix exhibited uniform oxide layer growth, most B_4C particles showed no significant corrosion. However, as shown in the figure below, some B_4C particles appeared to have undergone corrosion, though the frequency of occurrence was difficult to determine as shown in Fig 4. EDS analysis detected trace amounts of oxygen in the areas suspected of B_4C corrosion, along with a slight decrease in boron content. According to previous studies on the corrosion of B_4C powder, B_4C particles react with H_2O to form boron oxides [5].

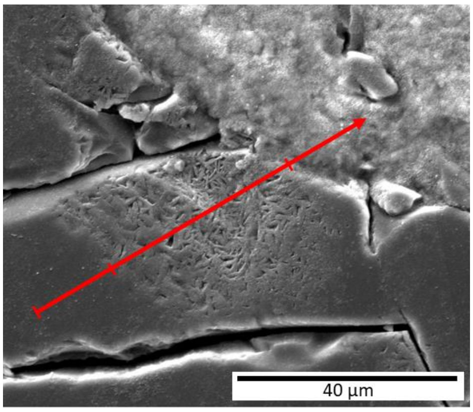

Fig. 4. Corroded B_4C surface image.

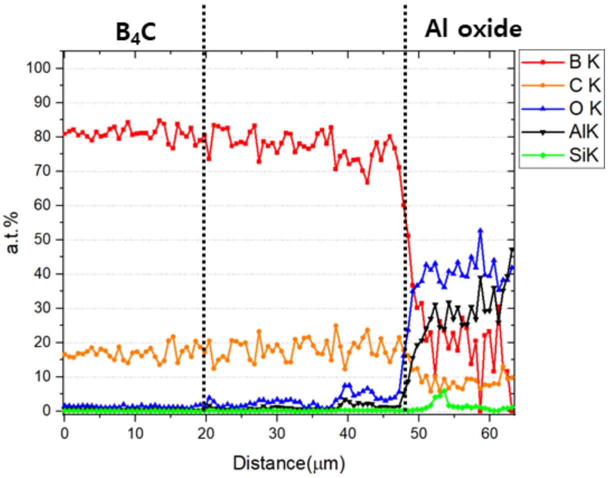

Fig. 5. EDS Results in Figure 4

From a thermodynamic perspective, the corrosion reaction of B_4C exhibits a higher Gibbs free energy than that of aluminum, indicating lower reactivity as shown in Fig 6. However, the initial corrosion of aluminum leads to the formation of a 2 μm thick oxide layer, which acts as a passivation layer, making B_4C particles relatively more vulnerable to the corrosive environment.

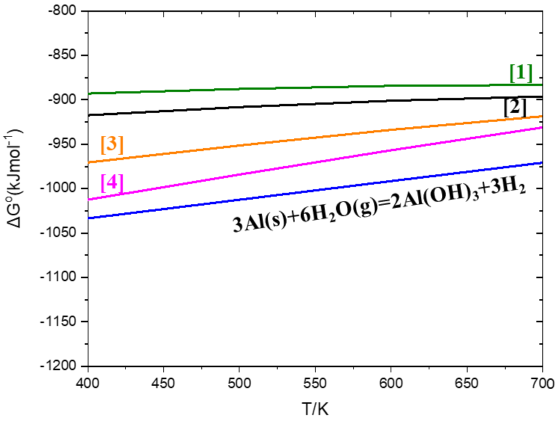

Fig. 6. Gibbs free energy according to B_4C, Al reaction

$$B_4C(s) + 8H_2O(l) = 2B_2O_3(l) + CO_2(g) + 8H_2(g) \cdots (1)$$
$$B_4C(s) + 7H_2O(l) = 2B_2O_3(l) + CO(g) + 7H_2(g) \cdots (2)$$
$$B_4C(s) + 6H_2O(l) = 2B_2O_3(l) + C(s) + 6H_2(g) \cdots (3)$$
$$B_4C(s) + 6H_2O(l) = 2B_2O_3(l) + CH_4(g) + 4H_2(g) \cdots (4)$$

3.2 EIS analysis

The corrosion resistance of an oxide layer growing in a corrosive environment is determined by the degree of ion penetration and dissolution between the corrosive environment and the material. Therefore, to evaluate the corrosion resistance of the oxide layer over time, Electrochemical Impedance Spectroscopy (EIS) was performed. A two-electrode method was applied for the electrochemical experiment, where the working electrode was the specimen under investigation, and the reference and counter electrodes were mesh Pt, which does not undergo corrosion reactions.

Each electrode was fabricated by welding Pt wire, and a zirconia two-hole tube was used to prevent interference between the electrode currents. The electrochemical cell was installed in the existing accelerated corrosion experiment autoclave, and the ends of each electrode were connected to an electrochemical test device for EIS analysis. The EIS frequency range was scanned from 10^{-2} to 10^5 Hz. EIS analysis was performed several times for reproducibility of the experiment.

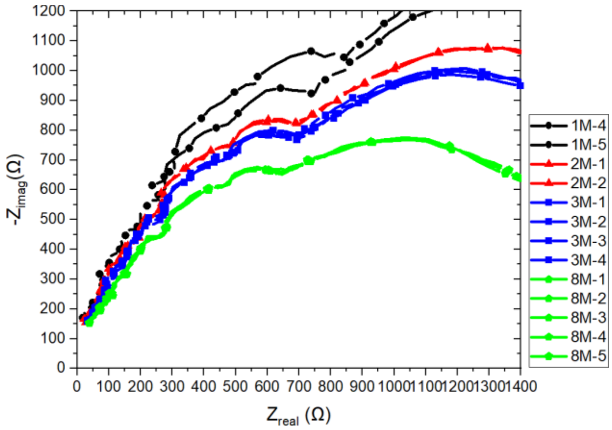

Fig. 7. Nyquist plot of accelerated corrosion experiment 1, 2, 3, 8 months specimens

Table IV: Electrical resistance value of Al6061-B4C according to the EIS result of Fig. 7

	$R_{solution}$ (Solution, Ω cm^2)	R_{SEI} (Solid Electrolyte Interphase, Ω cm^2)	R_{ct} (Charge Transfer Resistance, Ω cm^2)
1 month	0.002013	3722.67	1199.3
2 month	0.000015	2656	1322
3 month	0.010141	2446.75	1498.25
8 month	0.005786	1476.17	1958.17

As shown in Table IV, the EIS analysis results showed that the resistance of the test water (external electrolyte) was significantly lower than other resistance values. The R_{SEI} exhibited a decreasing trend over time, while the R_{ct} showed an increasing trend as time progressed.

The decrease in R_{SEI} over time indicates an increase in ion exchange between the oxide layer interface and the electrolyte, suggesting that the oxide layer thickness increased over time. On the other hand, the increasing trend in R_{ct} implies a reduction in charge transfer between the specimen interface and the oxide layer.[6] This is attributed to the formation of an Al_2O_3 passivation layer when the specimen was exposed to a corrosive environment, which enhanced its corrosion resistance.

3. Conclusions

An accelerated corrosion experiment was conducted to evaluate the long-term degradation of Al-B_4C neutron-absorbing materials. In the as-received specimens before corrosion, B_4C particles were embedded in the aluminum matrix. After conducting the accelerated corrosion experiment for eight months, an aluminum oxide layer of approximately 2 μm was uniformly formed, and although infrequent, some surface corrosion of B_4C was observed.

From a thermodynamic perspective, this phenomenon can be attributed to the preferential oxidation of aluminum, which has a lower Gibbs free energy, leading to the formation of an Al_2O_3 passivation layer. Subsequently, due to the formation of this passivation layer, the relatively weakened B_4C became more susceptible to corrosion.

According to the EIS analysis, the decrease in R_{SEI} over time indicates an increase in ion exchange between the oxide layer interface and the electrolyte, suggesting that the oxide layer thickness increased. The increasing trend in R_{ct} implies a reduction in charge transfer between the specimen interface and the oxide layer. This is because, when the specimen was exposed to a corrosive environment, an Al_2O_3 passivation layer was formed, enhancing its corrosion resistance.

Microstructural analysis also confirmed that no significant damage to the oxide layer occurred, indicating that the Al_2O_3 passivation layer on the specimen surface was uniformly formed without major defects. Therefore, no deterioration in corrosion resistance was observed.

ACKNOWLEDGEMENT

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REFERENCES

[1] Y. Jung, M. Lee, J. Kim, S. Ahn*, “10B(n, α)7Li reaction-induced gas bubble formation in Al–B4C neutron absorber irradiated in spent nuclear fuel pool“, Journal of Nuclear Materials 533 (2020).

[2] Ghali, Edward. (2010). Active and Passive Behaviors of Aluminum and Magnesium and Their Alloys. Corrosion resistance of aluminum and magnesium alloys : understanding, performance, and testing, (pp. 78-117). John Wiley & Sons, Inc., Hoboken, New Jersey

[3] Electric Power Research Institute (2005), “Handbooks on Neutron Absorber Materials for Spent Nuclear Fuel Application”, 1011818.

[4] H. P. Godard, The corrosion behavior of aluminum in natural waters(1960),

[5] Jonathan Brett Wierschke, (2015), Evaluation of Aluminum-Boron Carbide Neutron Absorbing Materials for Interim Storage of Used Nuclear Fuel, Doctor of Philosophy, University of Michigan.

[6] H.J. Greene and F. Mansfeld, Corrosion Protection of Aluminum Metal-Matrix Composites, CORROSION–Vol. 53, No. 12