

## **Assessment of Corrosion Characteristics for Graphite Composite in Boron-free Alkaline Solution**

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### **1. Introduction**

To reduce CO<sub>2</sub> emission as a reason of global warming, Korea aims to reduce 37% of CO<sub>2</sub> emission by 2030. One of the main ways to reduce CO<sub>2</sub> is to replace aging fossil power plants with eco-friendly power generation methods such as solar power, wind power, and nuclear power generation.

Therefore, Small modular reactor (SMR), which has a electrical power generation capacity less than 300 MW, has recently received great attention due to advantages in factory production, initial investment cost, flexible capacity expansion, mobility, etc.

SMR is being developed in about 80 types of reactors including integrated pressurized water reactors (i-PWRs), molten salt reactors, high temperature gas-cooled reactors, fast reactors, micro-reactors, etc. In addition, the majority of these is a i-PWR, which is cooled by light water. SMRs being developed in Korea such as SMART, ARA, i-SMR, and Bandi-60S, are also the type of i-PWR. Among them, i-SMR (innovative SMR), which has being developed to respond to various needs, employs various innovative technologies such as integrated main coolant pump (MCP) and control rod drive mechanism (CRDM) and boron-free chemistry. Then, the reactivity control of core is performed only by control rods due to the boron-free chemistry. In addition, frequent actuation of CRDM can cause seizing of the control rod and accelerate damage of the shaft and bearing materials.

Graphite or its composite has been employed as a material of bearing retainer or bearing in CRDM and MCP of pressurized water reactors due to its superior corrosion resistance and high-temperature durability, and low friction [3]. Therefore, this material is expected to be adopted as a constituent material of CRDM and MCP of SMRs. However, assessment of corrosion properties to ensure the integrity of these materials in an alkaline solution have been rarely.

Thus, we investigated the corrosion behavior of graphite composite, which is one of commercial bearing materials, under alkaline solution for 1000h at different temperature in this work. The corrosion rate was calculated from weight change of the specimens and the characteristics of oxide layer were investigated using scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), X-ray diffractometer.

### **2. Experiments**

Corrosion test specimens were machined with dimension of 24.5 mm x 15 mm x 2 mm from graphite composite block, a 3mm hole was machined at the top of each sample to hang on the specimen tree. In addition, the ID was marked on the top of specimens using a laser engraving machine to distinguish between the specimens.

The sample surface was finished using SiC paper of #600 and #1000 grit, consecutively. Corrosion test was conducted in the autoclave at four temperature conditions of 120, 180, 240, and 300°C with increase in test time. The alkaline solution was prepared by adding ammonia solution to deionized water, resulting in a pH of 10.5 at 25°C. In addition, the corrosion rate was assessed using the gravimetric method based on weight change measurement before and after tests.

The microstructure of corroded sample was analyzed through X-ray diffraction (XRD) equipment before and after corrosion test. The crystallographic information of the oxide layer was analyzed by scanning in the 2-theta range of 5° to 110° with a scan rate of 0.01°. The surface morphology of corroded sample was observed using SEM before and after the test. Furthermore, the chemical composition of the oxide layer was analyzed using EDS equipped with SEM.

### **3. Results and discussion**

Fig. 1. shows the corrosion rate of specimens tested at different temperature. Corrosion rate at 120, 180, and 240°C was evaluated in the range of -4 to 4 μg/cm<sup>2</sup>h regardless of test time and no particular tendency was observed according to the test time. However, the corrosion rate at 300°C negatively increased until 400 h, and then gradually decreased as the test time increased after 400 h. Considering the magnitude of the corrosion rate, it is thought that the graphite composite is hardly corroded in the alkaline solution, but dissolution occurs only at 300°C and the amount of corrosion increases slightly as the test time increases.

Fig. 2. presents SEM surface micrographs of specimens tested at 120 and 180°C, respectively, for 200 h. Some pores and white particles are observed in surface on both specimens. The pores observed on the surface are determined to have been formed during the manufacturing process of the graphite composite, but the white particles are expected to have been formed during the corrosion test.

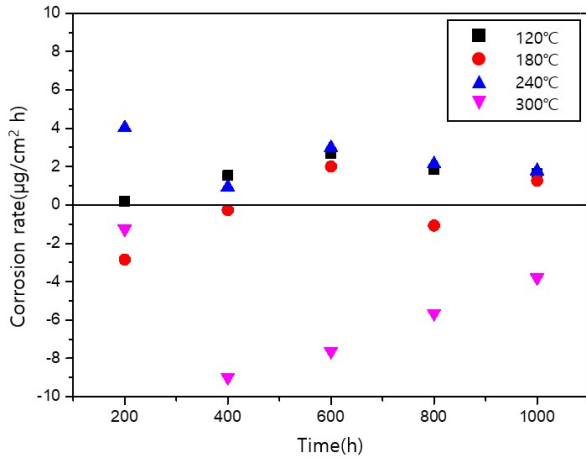


Fig. 1. Corrosion rate of graphite composite exposed at the temperature of 120, 180, 240 and 300°C with increase in test time.

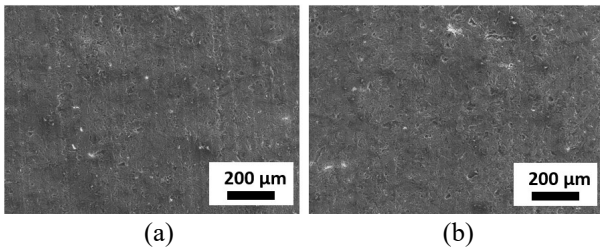


Fig. 2. SEM images of graphite composite specimens corroded at (a) 120°C and (b) 180°C, respectively, for 200 h.

In order to further analyze the chemical compositions on as-received and corroded specimens, the specimen untested and tested at 180°C were analyzed using SEM-EDS as shown in Fig. 3 and Table 1. A number of wrinkles are mainly observed on the surface of the as-received specimen, and white particles are observed inside the matrix as shown in Fig.3(a). However, polyhedral-shaped white particle was observed as shown in Fig.3(b). As a result of EDS point analysis, the specimen mainly consists of carbon and the small amount of S, O, Fe, Al, and Si were measured in a part of specimen. In particular, the much O and Ti contents were analyzed on the as-received surface at point 1 as shown in Fig.3(a). In addition, the content of Ni and Zn was newly analyzed on corroded specimen at point 3 as shown in Fig.3(b). These elements in point 1 and 2 are considered to have been included in the manufacturing process of the graphite composite. In addition, the polyhedral white particle having high Ni content at point 3 in Fig.3(b) is thought to be precipitated after dissolution during the corrosion process. This precipitate should be formed from Ni and Zn elements, which is added as a metal binder.

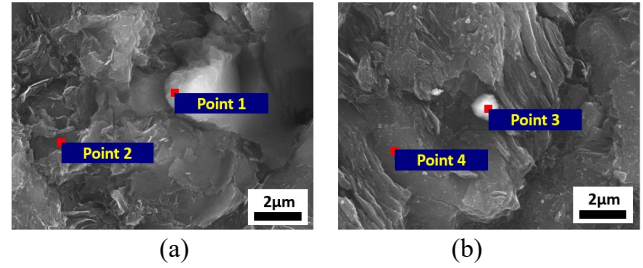
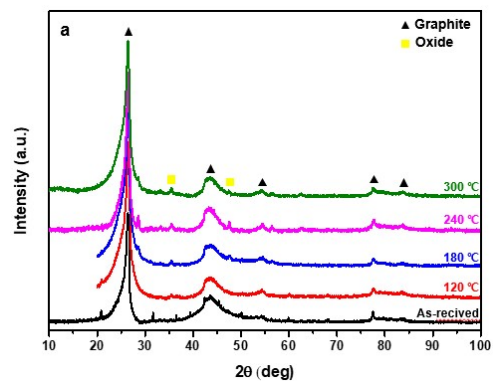


Fig. 3. SEM-EDS locations on (a) as-received and (b) corroded specimen at 180°C for 200 h.

Table. 1. Chemical composition analyzed in Fig. 3.

Element	Point 1		Point 2		Point 3		Point 4	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
C	67.3	76.4	90.0	94.0	76.6	92.3	97.2	98.4
O	24.8	21.2	5.2	4.1	1.3	1.2	1.5	1.1
S	0.5	0.2	1.4	0.5	5.6	2.5	1.3	0.5
Fe	0.2	0.0	0.3	0.1	0.2	0.0	0.1	0.0
Ni					16.0	3.9		
Zn					0.4	0.1		
Al	0.2	0.1	1.2	0.6				
Si	0.2	0.1	1.7	0.8				
Ti	6.8	1.9						
Total	100.0							

Fig. 4. shows XRD patterns of specimens tested at different temperature for 200h and 1000h, with as-received specimen. As-received specimen shows only the characteristic peaks of graphite. However, the characteristic peaks of graphite oxide newly appeared in corroded specimen at the temperature higher than 180°C. However, the change in XRD pattern is not observed between specimens tested for 200 h and 1000h. This is considered to be because the corrosion amount of the graphite composite is very low at all temperature conditions.



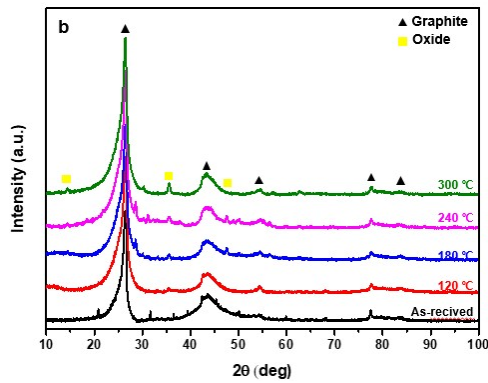


Fig. 4. XRD patterns of as-received and corroded specimens with increase in temperature for (a) 200 and (b)1000 h.

These results indicate that the graphite composite is difficult to be corroded in alkaline solution, particularly, at high temperature. Furthermore, it can be seen that there is little surface change during corrosion test. However, the metal or metal oxide particle can be formed by precipitation through the dissolution as shown in Fig.3. The result of corrosion rate as shown in Fig.1 means that the graphite composite is thermodynamically unstable in alkaline solution at 300°C.

#### 4. Conclusions

1. The effect of temperature on corrosion rate of graphite composite in alkaline solution is negligible, but its thermodynamic stability was somewhat weakened at 300°C.
2. The surface change after corrosion test is rarely observed and some precipitations are observed a part of surface.
3. The oxide phases such as carbon sulfur oxide and graphite oxide should be newly formed through corrosion in alkaline solution.

These findings suggest that graphite composite is not significantly degraded under alkaline primary coolant at temperature below 240°C. Considering that the actual operational temperature of CEDM is 120°C, it is expected that the graphite composite can be suitable in alkaline solution as a material for bearing.

#### ACKNOWLEDGEMENTS

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