

Corrosion Behavior of Graphite Composite in Alkaline Aqueous Solution

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1. Introduction

The Small modular reactor (SMR) has recently received great attention due to advantages in factory production, initial investment cost, flexible capacity expansion, mobility, etc. The integrated pressurized water reactors (i-PWR) has developed with employing various innovative technologies such as integrated main coolant pump (MCP) and control rod drive mechanism (CRDM) in order to respond to various needs. The innovative SMR(i-SMR) under development domestically has the characteristics of playing not only in-vessel MCP & CRDM but also a boron-free operation. The B-free operation, alkaline chemistry is applied in the design to ensure the integrity of materials. However, there is no integrity data for primary system materials in B-free chemistry conditions because it has no case which has been applied to the reactor coolant system. Therefore, it is necessary to obtain integrity evaluation data for primary system materials in simulated alkaline primary coolant condition. In particular the CRDM and MCP materials, which require more frequent operation than those in commercial NPP, it is important to obtain damage evaluation data in the operating environments.

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, lubricating effect 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), energy dispersive spectroscopy (EDS), X-ray diffractometer(XRD) and X-ray fluorescence (XRF).

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 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 chemical composition change was analyzed through XRF equipment before and after corrosion test. The surface morphology of corroded sample was observed using SEM before and after the test. Then, the sample surface was observed using Backscattered Electron (BSE) equipped with SEM to clearly distinguish between the matrix and oxide. Furthermore, the chemical composition of the oxide layer was analyzed using EDS equipped with SEM.

3. Results and discussion

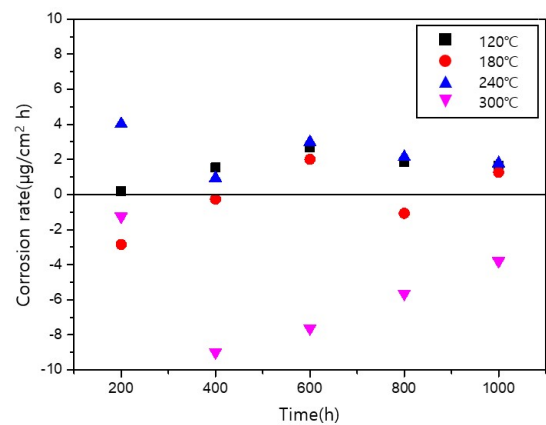


Fig. 1. Corrosion rate of graphite composite exposed at the temperature of 120, 180, 240 and 300°C with increase in test time.

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 -3 to 4 $\mu\text{g}/\text{cm}^2\text{h}$ regardless of test time and no particular tendency was observed with increasing the test time. However, all of the corrosion rate at 300°C shows negative value and it linearly increases after 400h test. 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.

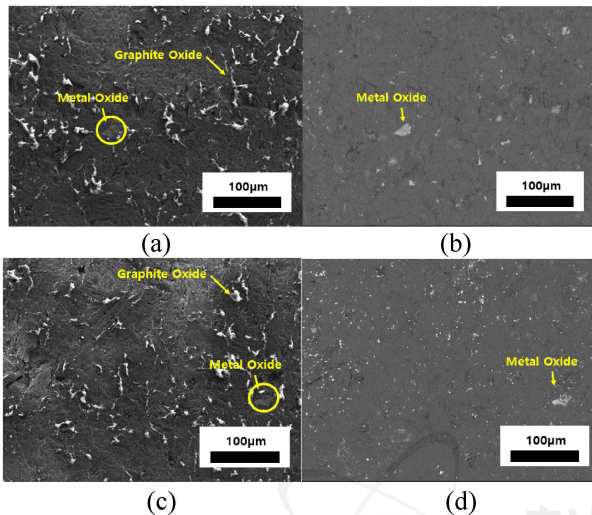


Fig. 2. SEM and BSE images of graphite composite specimens at as-received (a) SEM, (b) BSE image and corroded at 240°C for 1000h (c) SEM and (d) BSE image

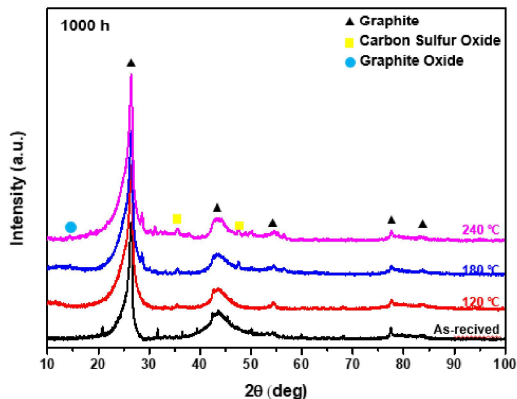


Fig. 3. XRD patterns of as-received and corroded specimens with increase in temperature for 1000 h.

Fig. 2. Presents the surface micrographs of as-received and corroded specimens tested at 240°C using by SEM and BSE. Some pores and white particles are commonly observed in surface on specimen. It is expected that these pores and white particles were formed during the manufacturing process of graphite composite, as clearly confirmed by BSE images. If the white particles were formed during the corrosion testing, and those were indeed metal oxides, as well distinguished in BSE and

SEM images. This indicates that the white particles are not metal oxide. In addition a white particle should be a graphite oxide from SEM and EDS data. This part will be discussed in more detail during the conference presentation.

The distribution of metal oxides exhibit similar patterns in the as-received specimen and corroded specimen at 300°C, as well as those at 120°C, 180°C, 240°C. While metal oxides in the as-received and 300°C samples are relatively uniformly distributed, other samples tend to cluster within and around pores.

Fig. 3. shows XRD patterns of specimens tested at different temperature for 1000h. All specimen were observed the graphite matrix and graphite oxide which were formed during the manufacturing process of the specimen. However, carbon sulfur oxide is detected in all corroded specimens. This indicates that sulfur plays a direct role in the corrosion process. And these result are supported by XRF and SEM-EDS analysis. Detailed on this topic will be provided during the conference presentation.

4. Conclusions

1. The effect of temperature on corrosion behavior of graphite composite in alkaline solution is negligible, except for that at 300°C due to its thermodynamic stability.
2. The oxides observed on the surface were the graphite oxide and carbon sulfur oxide identified by XRD analysis.
3. Graphite oxide was formed during the manufacturing process and change after corrosion tests is rarely observed. However, carbon sulfur oxide was observed the change after tests.

These findings means 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 around 120°C, it is expected that the graphite composite can be suitable in alkaline solution as a material for bearing.

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