Corrosion Behavior of Nickel-impregnated Graphite Material under Alkaline Primary Coolant in Small Modular Reactors

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1. Introduction

Graphite and its composite materials are used in variety applications such as industry, transportation, energy, defense, and medicine due to their characteristics such as high heat resistance, friction resistance, irradiation resistance, self-lubrication, and high thermal conductivity and electrical conductivity. In particular, graphite has been employed as various bearing materials in commercial pressurized water reactors (PWRs).

Recently, small modular reactors (SMRs), which have the electric capacity less than 300 MW, have had a great attention to be an eco-friendly power generation method to replace the aging fossil fuel reactor. SMR is classified by a variety of types such as integrated-PWR, molten salt reactor, high-temperature gas-cooled reactor, fast neutron reactor, and micro-reactor. However, most SMRs are being developed in the i-PWR type. Many SMRs of i-PWR type such as SMART, i-SMR, and Bandi-60S have also being developed in Korea.

Although the i-PWR was designed by integrating main components into one reactor vessel to improve economics and safety, it is expected that graphite material will still be used as a bearing material in SMR because it is placed in a similar water chemistry to commercial PWRs. Particularly, the i-SMR (innovative SMR) is designed to operate in an alkaline boron-free water chemistry [1]. However, the assessment on the corrosion behavior of graphite and its composite has rarely been made.

In this work, we investigate corrosion behavior of commercial nickel-impregnated graphite in alkaline chemistry condition to confirm the applicability in i-SMR system as the bearing materials.

2. Experimental methods

The graphite material, which is made including 4.15% Ni as a binding material and used as a bearing material in commercial PWR, was used as a test material. The chemical composition of this graphite material analyzed using XRF is summarized in Table 1.

Table 1. Chemical composition of graphite material

Element	С	Ni	0	Cr	Fe	Si
wt %	93.09	4.15	1.25	0.66	0.38	0.13

2.1 Specimen preparation

Specimens were machined with a dimension of 14.5 mm x 27.3 mm x 2 mm for corrosion test. A 3 mm hole was machined at the top of each sample to hang on the specimen tree. Each specimen was engraved with a unique number using laser marking equipment and its surface was finished using SiC paper of #600 grit and #1000 grit to control surface roughness. The specimens were subsequently cleaned in acetone, alcohol and deionized (DI) water.

2.2 Corrosion Test

Corrosion tests were performed at temperatures of 120° C, 180° C, 240° C, and 300° C for 1000 hours. The test solution was prepared by adding ammonia solution into DI water, with adjusting a pH to 10.5 at 25° C. The corrosion rate was evaluated from three specimens each test condition, with measuring weight change before and after testing.

2.3 Specimen Analysis

The microstructure of the corroded specimens was analyzed using X-ray Diffraction (XRD) equipment before and after the corrosion tests. The crystallographic information of the oxide layers was analyzed by scanning within the 2-theta range of $10 - 100^{\circ}$ at a scan rate of 0.01° .

The surface morphology of corroded specimens was observed using scanning electron microscope (SEM) before and after the corrosion test. In addition, the chemical composition of the specimens was measured using energy-dispersive X-ray spectroscopy (EDS), equipped with SEM.

3. Results and discussion

3.1 Initial Sample Characterization

Fig. 1. shows the surface SEM image of commercial graphite material. The white embedded phases were observed in the size of few micrometers to few hundred micrometers. Considering the XRF results in Table 1, these phases are predicted to be formed by precipitation

of nickel during heat treatment process. In addition, the black part should be a graphite phase.



Fig. 1. SEM image of as-received commercial graphite material.

3.2 Corroded Specimen Analysis

Fig. 2. shows the XRD patterns of as-received and corroded specimens tested at different temperatures. The characteristic peaks of graphite and nickel carbide were only observed on as-received specimen, while the characteristic peaks of graphite oxide (GO) and nickel oxalate (C_2NiO_4) were newly observed on specimens tested in alkaline solution at the temperature higher than 240°C.



Fig. 2 XRD analysis of as-received and corroded graphite specimens tested at different temperatures for 1000 h.

Fig. 3. displays the weight change per unit area of corroded specimens tested at different temperatures for 1000 h. The amount of weight change of corroded specimens tested at the temperature less than 240°C positively increases as a function of test times, but that of specimens tested at 300°C negatively increases and decreases after test for 600 h. Negative value in weight change means a weight loss, that is, dissolution in here. In other words, it indicates that the graphite materials can be dissolved in alkaline solution at 300°C until 600 h. However, considering the results in weight change and XRD data, it can be seen that the graphite material

is stable at the temperature less than 240°C and its weight increases due to oxidation of nickel or nickel carbide inclusions or formation of graphite oxide. However, it is believed that these phases affect the corrosion properties of graphite materials.



Fig. 3 Weight change of corroded graphite specimens as a function of test time at different temperatures in an alkaline solution.

4. Conclusions

The commercial graphite material is consisted of graphite carbon, nickel and some impurities such as Cr and Fe. The graphite material was stable in alkaline solution at the temperature less than 240°C for 1000 h, but was dissolved at 300°C. The graphite oxide and nickel oxalate were formed at the temperature higher than 240°C. In addition, it would be these phases affecting to corrosion properties of graphite material. Therefore, the graphite material should be an appropriate as a bearing material in SMR primary condition at the temperature less than 240°C.

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