

Effect of Temperature on Corrosion Behavior of Si₃N₄ in Alkaline Water

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1. Introduction

System-integrated modular advanced reactor (SMART), which is developed by KAERI for goals producing electricity less than 300MW and desalinating seawater, is a type of small modular reactor(SMR). The main design features of SMART are an integration of main components such as steam generator, pressurizer, and reactor coolant pump and an introduction of soluble boron-free reactivity control method [1]. The boron-free water chemistry has been considered in alkaline condition, which can be achieved by containing alkaline pH agent such as NH₃, LiOH, NaOH or ethanol amine (ETA) [2,3]. Among them, ammonia is a significant pH adjuster of SMR primary water due to its advantages in corrosion inhibition and deposition of corrosion products. Ammonia produces nitrogen and hydrogen by radiolysis in the core during operation, and the produce hydrogen is used to eliminate dissolved oxygen in primary coolant [4]. Evaluation of the corrosion behavior of structural materials in the primary water chemistry of pressurized water reactor (PWR) is important to secure the integrity of nuclear power plants. Thus, corrosion studies of candidate materials used for SMART design under ammonia water chemistry condition are demanded for ensuring the integrity of nuclear power plants along with optimized chemistry condition.

Silicon nitride (Si₃N₄), an representative engineering ceramic, has been used in various industries due to its excellent heat resistance, corrosion resistance, and wear resistance [5,6]. Hence, this material have being considered as a bearing material of main coolant pump in SMART.

In this work, the corrosion behavior of the material was evaluated in high temperature alkaline water including ammonia in order to confirm the applicability of Si₃N₄ to SMART.

2. Experiments

In this section, sample preparation, autoclave conditions for corrosion test, and analysis of oxide layer using scanning electron microscopy (SEM) and X-ray diffraction (XRD) were described.

A Si₃N₄ sample was machined with the dimension of 12 mm x 30 mm x 2 mm for corrosion test and a 3 mm hole was machined at the top of each sample to be placed in the sample holder. Thereafter, sample number was marked to distinguish each sample using a laser ablation equipment. Sample surface was finished using SiC paper with #600 and #2000 grit, respectively. Corrosion tests were carried out at the temperature of 120, 180, 240, and

300°C for 200 and 400 hours, respectively. The test solution was prepared by adding ammonia solution into deionized water and its pH was a 10.5 at 25°C. In addition, the corrosion rate was evaluated by gravimetric method measuring the weight change of the specimens before and after tests.

The microstructure of corroded specimens was analyzed through XRD analysis before and after the corrosion tests. The crystallographic information of the oxide layer was analyzed by scanning in the 2-theta range of 10° to 80° with scan rate of 0.01°.

The surface morphology of corroded specimens was observed using SEM analysis before and after the corrosion test. In addition, the chemical composition of oxide layer was analyzed using energy-dispersive X-ray spectrometer (EDS) equipped with SEM.

3. Results and discussion

Fig. 1 shows the pictures of Si₃N₄ specimens corroded at 120, 180, 240 and 300°C, respectively, for 200 hours. The color of corroded specimen is changed from dark gray to bright gray with increase in test temperature. However, the specimen corroded at 300°C was deviated from this color change trend. The specimen tested at 300°C shows dark gray color with many spots. In addition, the spalling in a part of the surface was observed. This is presumably a phenomenon occurred by the shrinkage stress when the surface oxide layer containing moisture is dried. In addition, it might be that the color change of specimen surface is caused by degree of oxidation [4].

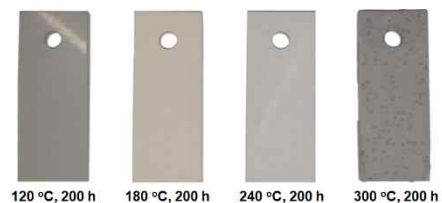


Fig. 1. Pictures of Si₃N₄ specimens corroded at 120, 180, 240 and 300 °C, respectively, for 200 hours.

Fig. 2 shows the graph for weight loss of Si₃N₄ corroded at different test temperature in alkaline solution. The weight loss of Si₃N₄ specimen gradually increases with increase in test temperature. In particular, the weight loss of Si₃N₄ tested at the temperature higher than 180°C increased by about two times. The effect of test temperature on weight change of the specimen tested for 400 hours shows a similar trend to that of the specimen for 200 hours, but it showed an increase of more than double. These results indicate that the test temperature

and time are an influence factor on the corrosion of Si_3N_4 in alkaline solution.

Fig. 3 shows the XRD patterns of Si_3N_4 specimens corroded at different temperature for 200 hours. The characteristic peaks of tested specimens were mainly corresponded with that of $\beta\text{-Si}_3\text{N}_4$ and $\alpha\text{-Si}_3\text{N}_4$. The halo intensity increases between 10° and 30° at 2-theta values due to amorphous SiO_2 formed in the specimen corroded above 240°C . In addition, the change in characteristic peaks was not observed with increase in test temperature.

Fig. 4 shows the SEM-EDS result on the as-received specimen and the specimen corroded at 300°C for 200 hours. The surface morphology of corroded specimen became rougher than that of as-received specimen. In addition, the nitrogen concentration on the surface of specimen severely decreased after corrosion test, while the oxygen concentration increased. This is probably because of oxidation of Si_3N_4 in an alkaine solution.

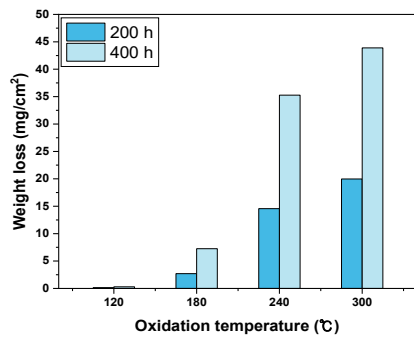


Fig. 2. Weight loss of Si_3N_4 after corrosion tests in the alkaline solution.

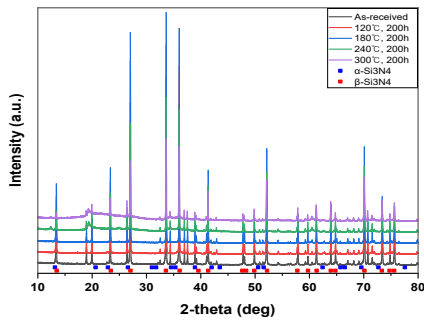


Fig. 3. XRD patterns of Si_3N_4 specimens as-received and corroded at different temperature for 200 hours.

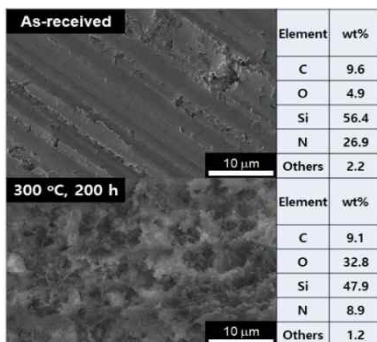
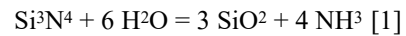


Fig. 4. SEM-EDS analysis on Si_3N_4 specimens as-received and corroded at 300°C for 200 hours.

4. Conclusions

1. The weight loss of Si_3N_4 specimen was gradually increased with increase in test temperature and test time in alkaline solution. In particular, the weight loss of Si_3N_4 specimen was abruptly increased at the temperature higher than 240°C and the spillings on the specimen corroded at 300°C were observed.
2. Based on the XRD and SEM-EDS results, it is concluded that amorphous SiO_2 was formed on the specimen surface during corrosion test according to the following equation [1].



3. This indicates that the Si_3N_4 is unsuitable in higher temperature than 240°C in alkaline primary water condition due to oxidation and spalling.

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