Effect of pH control agents on magnetite deposition on steam generator tubing

Ji-Min Lee, Soon-Hyeok Jeon, Kyeong-Su Kim, Do Haeng Hur*
Safety Materials Technology Development Division, Korea Atomic Energy Research Institute, Daejeon, Korea
**Corresponding author: dhhur@kaeri.re.kr*

1. Introduction

The sludge deposited on the secondary side of steam generator tubes is composed of more than 90 percent of magnetite, and the rest consists of jacobsite and trevorite [1]. These deposits can reduce the thermal efficiency of a pressurized water reactor (PWR) and enhance the corrosion of secondary side materials due to the galvanic effect [2]. Therefore, mitigating magnetite deposition is one of the main goals for water chemistry control.

In the secondary side, a pH value is a primary parameter affecting the erosion-corrosion wear rate and corrosion products release of the structural materials of steam generator [3]. Several pH control agents such as ethanolamine, morpholine, ammonia, and dimethylamine have been widely used [3]. Generally, operating pH values range from 9.2 to 9.8 depending on the nuclear power plant [4].

This study began with the idea that these various pH agents may be tightly related to the magnetite deposition behavior. In this study, effect of two pH agents (ethanolamine, ammonia) on the amount of magnetite deposited on the commercial steam generator tubes under the conditions similar to operating steam generators at a pH value of 9.0.

2. Experimental

Fig. 1 shows a schematic diagram of magnetite deposition loop that can simulate the secondary side conditions of a steam generator. As shown in the figure, the loop consists of three main components: a water tank, a Fe source tank, and a test section. Deionized water stored in the water tank was recirculated at a flow rate of 260 ml/min through the specimen equipped test section. The pH value was controlled to be 9.0 by injecting ethanolamine or ammonia solution into the water tank. The Fe-acetate solution was stored in the Fe source tank and the solution was injected into the bottom of the test section at a flow rate of 1 ml/min. The specimen was a commercial Alloy 690TT tube with one end welded and an internal heater inserted inside. The pressure in the test section was 60 bar and the temperature was about 270 ℃. Each test lasted 14 days and the dissolved oxygen was maintained below 5 ppb.

Fig. 2 shows the steam generator tube specimen before and after the test. After the test was finished, the specimen was dried at 60 ℃ for about 3 hours and then cut with a low speed cutter for analysis. The cross-section of the magnetite deposits was observed by focused ion beam (FIB). To evaluate the amount of magnetite, the specimen was cut to about 2 cm in length and then immersed in a chemical cleaning solution at 93 ℃ for 12 hours. Finally, the concentration of iron dissolved in the chemical cleaning solution was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the amount of magnetite deposited per unit area was calculated.

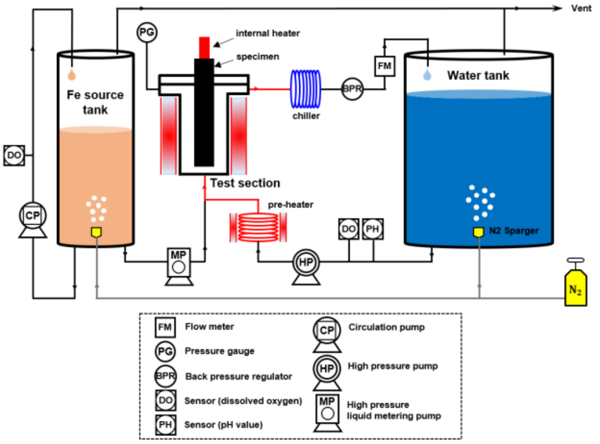

Fig. 1. A schematic diagram of magnetite deposition loop which can closely simulate the secondary side conditions of a steam generator.

Fig. 2. Commercial steam generator tube (Alloy 690TT) used in this study (a) before and (b) after the experiment.

3. Results and Discussion

Fig. 3(a) and 3(b) show cross-sectional morphologies of the magnetite deposited on the Alloy 690TT tube surfaces when ethanolamine and ammonia are used as a pH agent, respectively. As shown in the figure, the magnetite layer has numerous pores and is similar to the sludge flakes obtained from the tube surfaces of an actual steam generator [1]. Interestingly, more pores were observed when ammonia is used as a pH agent. This may be due to the fact that ammonia has lower boiling point and higher volatility than ethanolamine. The average thickness of the magnetite deposits was about 35 μm and about 13 μm in Fig. 3(a) and 3(b), respectively.

Future investigation will be performed on the distribution of pore size and two-dimensional porosity.

In addition, to compare the properties of the magnetite deposits based on the pH agent, the grain size and crystallographic orientation using electron backscattered diffraction (EBSD) will be analyzed later.

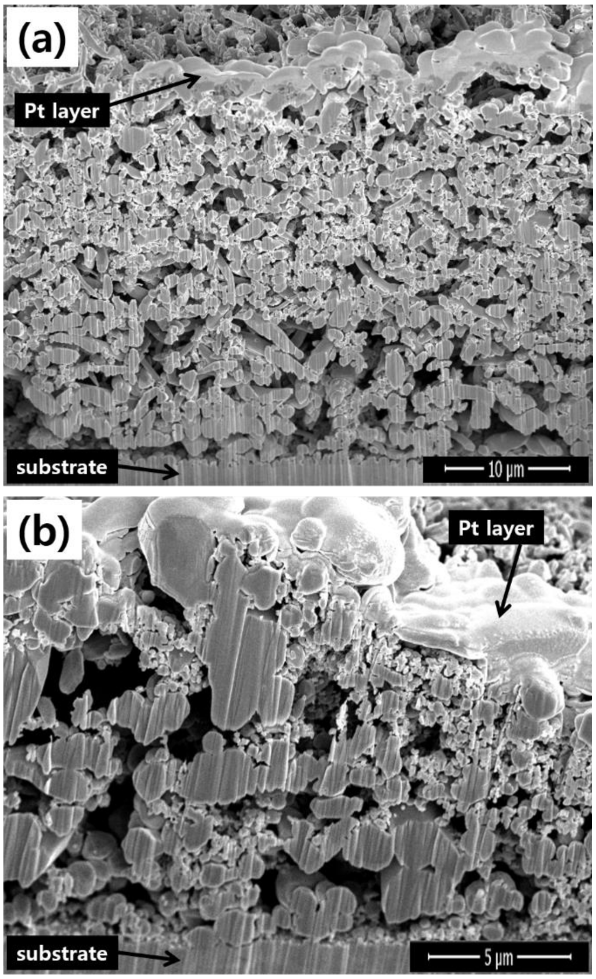

Fig. 3. Cross-sectional morphologies of the magnetite deposited on the Alloy 690TT tube surfaces when (a) ethanolamine and (b) ammonia is used as a pH agent.

Figure 4 shows the amount of magnetite per unit area deposited on the Alloy 690TT tube depending on the pH agents at a pH of 9.0, with an uncertainty of 2%. As shown in the figure, the use of ethanolamine as a pH agent results in 1.52 times more magnetite deposition than ammonia.

A previous study has shown that particle deposition is strongly governed by the particle's surface charge, i.e., zeta potential [4]. Our results will be further discussed by measuring both the zeta potential of magnetite particles and the zeta potential of the surface of steam generator tubes in ethanolamine and ammonia solution.

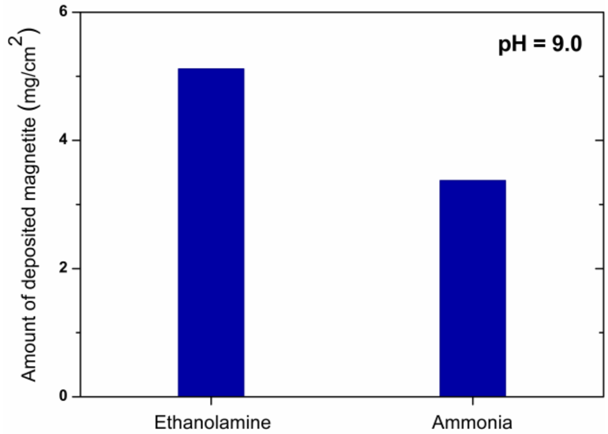

Fig. 4. The amount of magnetite deposited per unit area depending on pH control agents at a pH value of 9.0.

4. Conclusions and Future studies

(1) Magnetite deposited on the surface of Alloy 690TT tubing has numerous pores and is similar to the actual morphology from an operating steam generator.
(2) At a pH value of 9.0, the amount of magnetite deposits was 1.52 times higher in the case of using ethanolamine as a pH agent than in the case of using ammonia.
(3) The properties of the deposited will be compared by analyzing porosity, grain size, and so on. In addition, both the zeta potentials of magnetite particles and the steam generator surface will be measured to describe the magnetite deposition behavior based on the pH agents.

5. Acknowledgements

This work was supported by the National Research Foundation (NRF) grant of the Republic of Korea funded by the Korean government (NRF-2017M2A8A4015159).

REFERENCES

[1] S. H. Jeon, S. M. Hong, H. C. Kwon, D. H. Hur, Characteristics of steam generator tube deposits in an operating pressurized water reactor, Journal of Nuclear Materials 507 (2018) 371-380.
[2] G. D. Song, S. H. Jeon, Y. H. Son, J. G. Kim, D. H. Hur, Galvanic effect of magnetite on the corrosion behavior of carbon steel in deaerated alkaline solutions under flowing conditions, Corrosion Science 131 (2018) 71-80.
[3] V. F. Tyapkov, S. F. Erpyleva, Water Chemistry of the Secondary Circuit at a Nuclear Power Station with a VVER Power Reactor, Thermal Engineering, 2017, Vol. 64, No. 5, pp. 357-363.
[4] J. Essi, S. Konsta, S. Timo, Determining Zeta Potential of Magnetite Particles in PWR Secondary Side Water Treated with Ammonia or Ethanolamine by Using Streaming Potential Technique, 20th NPC International Conference, Brighton, UK, Oct. 2-7, 2016.