A Study on NF_3-Ar Plasma Etching Reaction with Cobalt Oxide on Stainless Steel

Jae-Yong Lee, Kyung-Min Kim, You-Jin Kang, Yong-Soo Kim*
Department of Nuclear Engineering, Hanyang University,
222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Korea
**Corresponding author: yongskim@hanyang.ac.kr*

1. Introduction

The permanent shutdown and decommissioning of NPPs (nuclear power plant) has been growing steadily in the world after Fukushima accident. According to IAEA, the number of the shutdown of NPPs is totally 194 in the world [1]. In the Korea, there are 24 operating NPPs, 4 NPPs under construction and 2 shutdown NPPs. Especially, Kori-1 and Wolsong-1 have permanent shutdown and 10 NPPs will come to end of lifetime as 40 years until 2029 based on NPPs lifetime.

But, Korea has only experience on decommissioning of research reactor, TRIGA MARK-3. Therefore, government, research institute, university and industry have conducted development of various technologies and regulations related decommissioning of NPPs.

The management of radioactive waste generated decommissioning of NPPs is important issues. Because, according to literature of decommissioned NPPs, period and cost for decommissioning of NPPs are impacted by radioactive waste. As shown in table I, most radioactive waste of decommissioning consists of metal and concrete at PWR with power capacity of 900 - 1300 MWe.

Table I: Typical radioactive waste generated from decommissioning at PWR (900 – 1300 MWe) [2]

Radioactive waste	Volume (ton)
Activated steel	650
Activated concrete	300
Contaminated ferrite steel	2,400
Steel likely to be contaminated	1,100
Contaminated concrete	600
Contaminated lagging	150
Contaminated technological	1,000

Also, it is predicted that most of radioactive waste consists of metal and concrete at Kori-1.

Table II: Estimated initial volume of radioactive waste at Kori-1 [3]

Class	Type	Volume (m^3)
CW	Cable	354
	Piece of concrete	112,954
	Toxic wastes	25
	Asbestos	366
	Large component	2,282
	Small metals	23,546
	Spent fuel storage rack	0
ILW	Small metals	8
	Resin or filter	15
LLW	Cable	22
	Piece of concrete	229
	Scabbled concrete	34
	Dry active waste	409
	Toxic waste	11
	Asbestos	12
	Large components	832
	Reactor vessel	199
	Small metals	3,416
	Spent fuel storage rack	490
	Resin or filter	19
VLLW	Cable	83
	Piece of concrete	187
	Scabbled concrete	100
	Toxic wastes	22
	Asbestos	129
	Small metals	6,308
	Spent fuel storage rack	0
	Resin or filter	0

Accordingly, if a decontamination technique can effectively remove contaminants from wastes of metal and concrete, base materials can be treated as non-radioactive and reused or recycled, which leads to effective volume reduction.

Therefore, in this study, in order to demonstrate the high etching rate of stainless steel 316 with radioactive Co isotopes, plasma etching reaction of cobalt oxide film grown on stainless steel 316 was examined using NF_3-Ar gas.

2. Experimental

2.1 Preparation of Cobalt Oxide on Specimen

First, to prepare the cobalt oxide films on base metal using stainless steel 316. Disc specimen polished with 320, 600 and 1200 grain sandpaper and cleaned mixed solution using methanol and acetone in ultrasonic cleaner. Cobalt nitrate (II) hexahydrate solution with a concentration of 100 mg/mL was applied on their surfaces. Next, samples were baked in an electrical furnace to grow cobalt oxide films on the surface of the stainless steel 316.

2.2 Design of Plasma Etching Equipment

The sample was heated to 800 ℃ by heater and RF power up to 600 W at 13.56 MHz was applied in reaction chamber. A cold trap was installed in the chamber to collect reaction product for its identification.

2.3 Plasma Etching Experimental

Total pressure in the reaction chamber was maintained 0.3 torr and the total flow rate of NF_3 gas and Ar gas was fixed at 20 sccm (standard cubic centimeters per minute). Etching rate was determined by converting the weight loss of specimen during reaction to remove thickness of surface. Surface analysis of samples was conducted using SEM (Scanning Electron Microscopy) and XPS (X-ray Photoelectron Spectroscopy).

3. Result & Discussions

3.1 Observation of Surface before and after reaction

SEM show that cobalt oxide film removed from the surface of specimens after plasma etching reaction (Fig. 1).

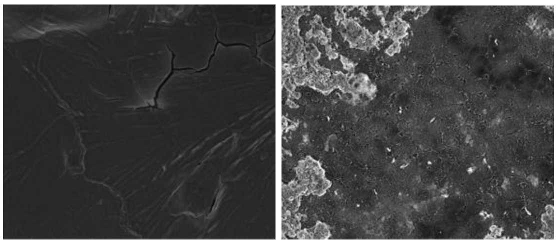

Fig. 1. Surface image of cobalt oxide film grown stainless steel before and after reaction using SEM

3.2 Analysis of Reaction Product

XPS analysis show peak of Co_{2p} binding energy at 780.1 eV, demonstrating that Co_3O_4 film formed on the surface of specimen (Fig. 2).

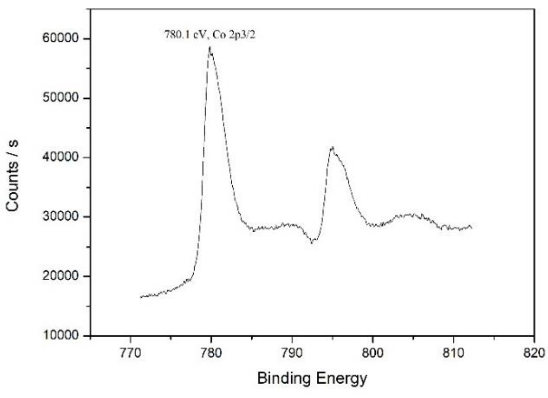

Fig. 2. Cobalt oxide film on the surface of specimen using XPS

To confirm the chemical form of the reaction product, XPS analysis of reaction product collected using a cold trap was performed. The result of XPS for Co_{2p} binding energy was 782.9 eV, while the binding energies of cobalt fluoride are known (Fig. 3).

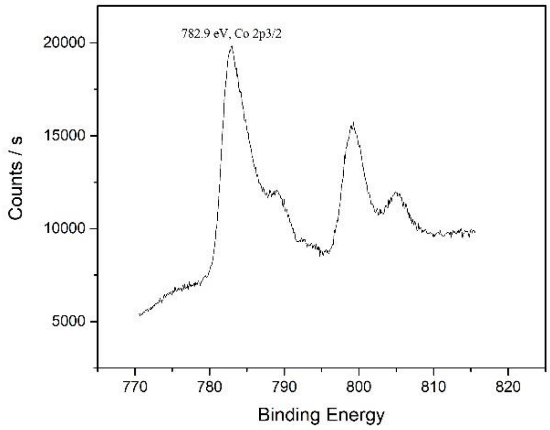

Fig. 3. Reaction product collected in cold trap using XPS

3.3 Plasma Etching Rate of Cobalt Oxide

In this experiment, it was founded that the cobalt oxide on specimen has different etching rate with different composition of NF_3-Ar gas in plasma reaction.

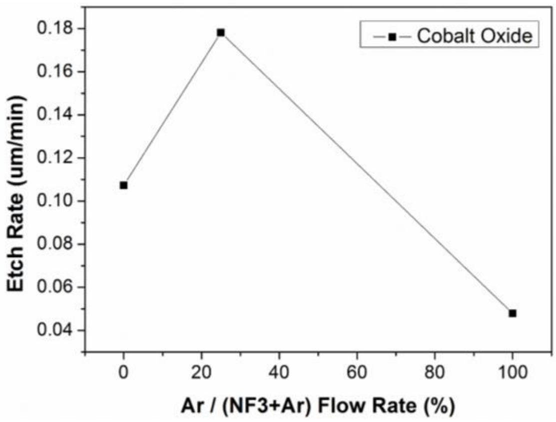

Fig. 4. Etching rate of cobalt oxide on specimen at different composition of NF_3-Ar gas in plasma reaction

Based on results of XPS analysis, Co_3O_4 film on surface of materials was removed by forming volatile reaction product of CoF_2.

$$Co_3O_4 + 6F \rightarrow 3CoF_{2(g)} + 4O$$

4. Conclusions

In this study, plasma etching demonstrate that the technique can be applied to efficiently and effectively remove major radioactive surface contaminants such as ^{60}Co.

Acknowledgements

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP: Ministry of Science, ICT, and Future Planning) (No. NRF-2017M2B2B1072888) and the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20191510301300)

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