Decontamination of Co, Mo by Ion-Assisted SF_6/O_2 Plasma

Sang-pil Yun,a Yong-soo Kim,a Sang-hwan Jeon,b Seung-hoon Lee,b Sung-nam Koh,b Dae-hyeon Cha,b
a Nuclear Engr. Dept., Hanyang Univ., Seoul, 133-791, Korea, yongskim@hanyang.ac.kr
b Joongang Inspection Co., Ltd,654-15, Sinsa-Dong, Gangnam-Gu, Seoul, 135-897, Korea

1. Introduction

Experimental research on the surface cleaning of metallic specimen using SF_6/O_2 plasma is carried out. To enhance the reaction rate, dc bias voltage is applied to the specimen. In this experiment the applicability and effectiveness of plasma decontamination processing are demonstrated. Metallic Co and Mo, the principal contaminants in the spent nuclear components, are chosen as specimens. Results show that the reaction rate of molybdenum is 10.21 *u*m/min. at 290 ^oC. In the case of cobalt, etching reaction hardly takes place at low temperatures. However, it begins to increase as temperature exceeds 350 ^oC. The reaction rate is 2.56 *u*m/min. at 420 ^oC.

OES analysis reveals that the intensities of F atom and CO molecule reach maximum at the optimum gas composition, which demonstrates that the primary reaction mechanism is fluorination and/or carbonyl reaction. To support these results, SEM and AES analysis are followed. And ion-assisted reaction is under conduction.

2. Methods and Results

Plasma reactor is a diode type and r.f. (13.56 MHz) power up to 600 W can be applied between the parallel electrodes. DC negative bias (-500 V, 1 A) can be applied to the substrate (Figure 1). The distance between them remains 10 cm during the current experiments. Sample can be heated up to 1200°C with halogen heater. Mass flow controller can control finely and flow rate remains 50sccm. Total gas pressure inside chamber is maintained at around 0.45 Torr during experiments.

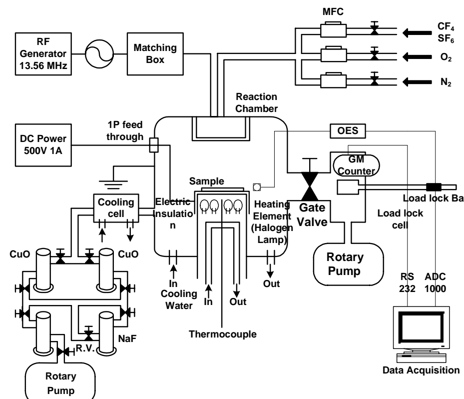


Figure 1. Schematic of Plasma reaction apparatus.

2.1 Sample Preparation

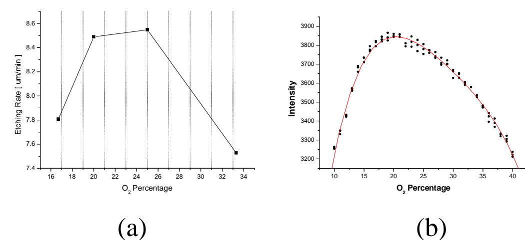
Non-radioactive metal samples (Co, Mo) with 99.8% purity are used as specimens. Specimens are manufactured to a thin disk of 0.7mm thickness from rod 10 mm and 5mm each radius using low-speed diamond cutter. Prior to the sample loading, the surfaces of the specimens are polished as mirror-like by 1200 grit SiC paper, cleaned with ultrasonic cleaner and baked at 200 °C for 10 minutes in a vacuum to evaporate the absorbed moisture on the surface.

2.2 Experimental Procedure

Experimental parameters are remained at 220 W r.f., of RF power, 0.45 Torr of pressure and 30 min. of reaction time at all experiments. First of all, Mo etching rate is measured to find the most efficient reaction rate of SF_6/O_2 plasma under changing O_2 ratio. In the most efficient O_2 ratio, etching rate of each specimen is measured as temperature. Etching rate is determined by weight loss measurement before and after the reaction with an electro-micro balance (BP210D, Satorius) whose sensitivity limit is 10^{-5}g. Weight loss is expressed in *u*m/min. OES (Optical Emission Spectroscopy) analysis is accompanied with the main experiments to diagnose and determine the plasma parameters and thus to understand the reaction mechanism.

At the same condition, negative bias is applied. This experiments are under conductuin.

Figure 2 shows that the most efficient O_2 rate of SF_6/O_2 plasma is about 25 %. Result that fluorine quantity is the maximum from OES analysis when O_2 rate is 20 % appears that essential reaction of the surface is fluorination reaction.

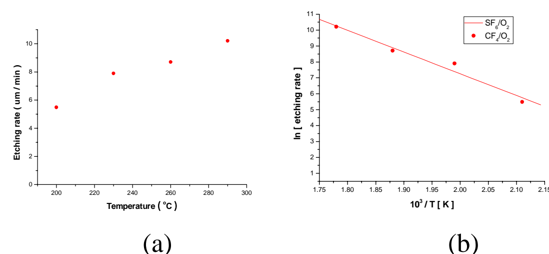


(a) (b)

Figure 2. (a) Etching rate of Mo as O_2 percentage at 260 °C SF_6/O_2 plasma (b) OES analysis about RF plasma as O_2 percentage.

2.3 Experimental Results

Etching rate is measured as temperature using SF_6/O_2 in 20% O_2 ratio and increase as temperature (Figure 3.).

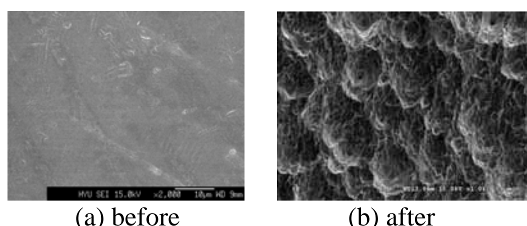


(a) (b)

Figure 3. (a) Etching rate of Mo as temperature at SF_6/O_2 plasma. (b) Arrhenius plot

Reaction speed is expressed by basic thermodynamic equation k = a exp $(-E_a/RT)$, k is reaction rate, E_a is activation energy. Plot shape is appeared linearly by changing results with Arrhenius plot. Activation energy is 14.932 KJ/mol.

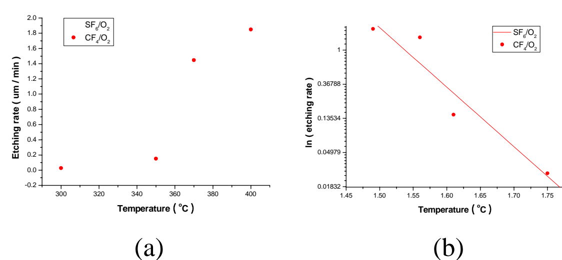
In Results of SEM analysis before and after, we can confirm the intensive reaction of surface (Figure 4)



(a) before (b) after

Figure 4. SEM analysis of Mo before and after the reaction at 290 °C SF_6/O_2 plasma (× 10K)

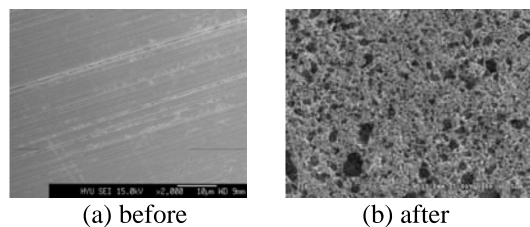
The etching rate of Co metal is very low (< 0.03 *u*m/min) below 350 °C temperature. Above 350 °C the reaction takes place. From Arrhenius plot, activation energy is 144.8 KJ/mol.(Figure 5.)



(a) (b)

Figure 5. (a) Etching rate of Co as temperature at SF_6/O_2 plasma (b) Arrhenius plot

SEM analysis at 400 °C shows that reacted surface get rougher after the reaction (Figure 6.).



(a) before (b) after

Figure 6. SEM analysis of Co before and after the reaction at 400 °C SF_6/O_2 plasma (× 10K)

3. Conclusion

Metallic Mo and Co surfaces etching using SF_6/O_2 r.f. plasma are carried out to demonstrate the feasibility of plasma decontamination processing. Reaction is the most efficient at 25 % O_2 percentage. Under the same conditions, negative bias applying experiments are being carried out. In the negative DC bias induced experiment more enhanced reaction rate is expected. The molybdenum reaction rate is 10.21 *u*m/min. at 290 ^oC and cobalt is 2.56 *u*m/min. at 420 ^oC.

OES analysis reveals that the intensities of F atom and CO molecule reach maximum at the optimum gas composition, which demonstrates that the primary reaction mechanism is fluorination and/or carbonyl reaction.

REFERENCES

[1] J.W. Coburn and H.F. Winters, Ion-and Electron-Assisted Gas-Surface Chemistry An Important Effect in Plasma Etching, J. Appl. Phys., 50, 5 (1979) 3189.

[2] Y.S. Kim, Y.D. Seo, M. Koo, Decontamination of Metal Surface by Reactive Cold Plasma Removal of Cobalt, J. Nucl. Sci. Technol., 41 (2004) 1-6

[3] Kaken, Inc. Mito-Institute, Ibaraki Univ., Japan, Newly Developed Decontamination Technology Based on Gaseous reactions Converting to Carbonyl and Fluoric Compounds, Nuclear Technology V. 124, (1998)

[4] Alfred Frill, Cold Plasma in Materials Fabrication, IEEE Press, New York, (1994).

[5] D.M. Manos, D.L. Flamm, Plasma Etching, Academic Press, (1988)

[6]Y. S. Kim, S. H. Jeon and C. H. Jung Fluorination reaction of uranium dioxide in $CF_4/O_2/N_2$ r.f. plasma : Annals of Nuclear Energy, Volume 30, Issue 11, July 2003, Pages 1199-1209

[7] L. Jiang, N.O.V. Plank, R. Cheung, Surface characterization of inductively coupled plasma etched SiC in SF_6/O_2 Mircoelectronic Engineering 67-68 (2003) 369-375

[8] I.A. Buyanova, A. Henry, B. Monemar : Photoluminescence characterization of SF_6-O_2 plasma etching of silicon , Material Science and Engineering B36 (1996) 100-103