A STUDY ON DECONTAMINATION OF TRU, Co, and Mo USING PLASMA SURFACE ETCHING TECHNIQUE

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Key Word: Decontamination, Radwaste, Plasma processing

ABSTRACT

Recently dry decontamination/surface-cleaning technology using plasma etching has been focused in the nuclear industry. In this study, the applicability and the effectiveness of this new dry processing technique are experimentally investigated by examining the etching reaction of UO_2, Co, and Mo in r.f. plasma with the etchant gas of CF_4/O_2 mixture. UO_2 is chosen as a representing material for uranium and TRU (TRans-Uranic) compounds and metallic Co and Mo are selected because they are the principal contaminants in the spent nuclear components such as valves and pipes made of stainless steel or inconel.

Results show that in all cases maximum etching rate is achieved when the mole fraction of O_2 to CF_4/O_2 mixture gas is 20 %, regardless of temperature and r.f. power. In case of UO_2, the highest etching reaction rate is greater than 1000 monolayers/min. at 370¡É under 150 W r.f. power which is equivalent to 0.4 ¥ìm/min. As for Co, etching reaction begins to take place significantly when the temperature exceeds 350¡É. Maximum etching rate achieved at 380¡É is 0.06 ¥ìm /min. Mo etching reaction takes place vigorously even at relatively low temperature and the reaction rate increases drastically with increasing temperature. Highest etching rate at 380¡É is 1.9 ¥ìm/min.

According to OES (Optical Emission Spectroscopy)_analysis, primary reaction seems to be a fluorination reaction, but carbonyl reaction may assist the dominant reaction, especially in case of Co and Mo.

Through this basic study the feasibility and the applicability of plasma decontamination technique may be demonstrated. Future works have been planned and thus more fundamental and practical studies will be carried out.

INTRODUCTION

Dry decontamination/surface-cleaning technology using plasma etching has been focused in the nuclear industry. The parts and equipment of the primary circuit in the nuclear power plant can be contaminated by the absorption or the adsorption of uranium compounds, transuranic (TRU) elements, corrosion products such as Co, Fe, Ni, Cr produced in the aqueous corrosion, and fission products such as Mo, Tc, Ru, Rh. If the contaminants on the surface of the parts and equipment can be removed selectively with this plasma decontamination technique it is possible to preserve or recycle the substrate materials, leading to the tremendous reduction of radioactive waste and economical gain by reducing the number of processing steps.

In this study, the applicability and the effectiveness of the new dry processing technique are experimentally investigated. For this examination, UO_2 is chosen as a representing material for uranium and TRU compounds and metallic Co and Mo are selected as representatives of the corrosion and fission products, respectively.

The fluorination of uranium dioxide has been extensively studied in the application-oriented fields such as uranium separation, processing, and conversion[1-4]. Along with the applied research, fundamental studies of UO_2/F_2 reaction have been reported by several authors[5-10]. Recently feasibility of burning spent PWR fuel in a CANDU reactor was carried out, whose main processes are to make re-sinterable fuel powder by decladding the spent fuel pins and dry-processing the burned uranium dioxide[11,12]. In this process, however, even the most candidate mechanical decladding techniques were unable to recover more than 98 to 99.5% of the heavy metal/metal oxide. A part of the remainder may be present as adherent dust and/or chemically bonded to the zirconium oxide layer on the inner surface of the fuel pin. Thus, additional removal process has been required to meet the criteria of 99.9% removal. For this secondary dry process, plasma processing technique using fluorine containing gas plasma was proposed and its applicability has been demonstrated[13,14].

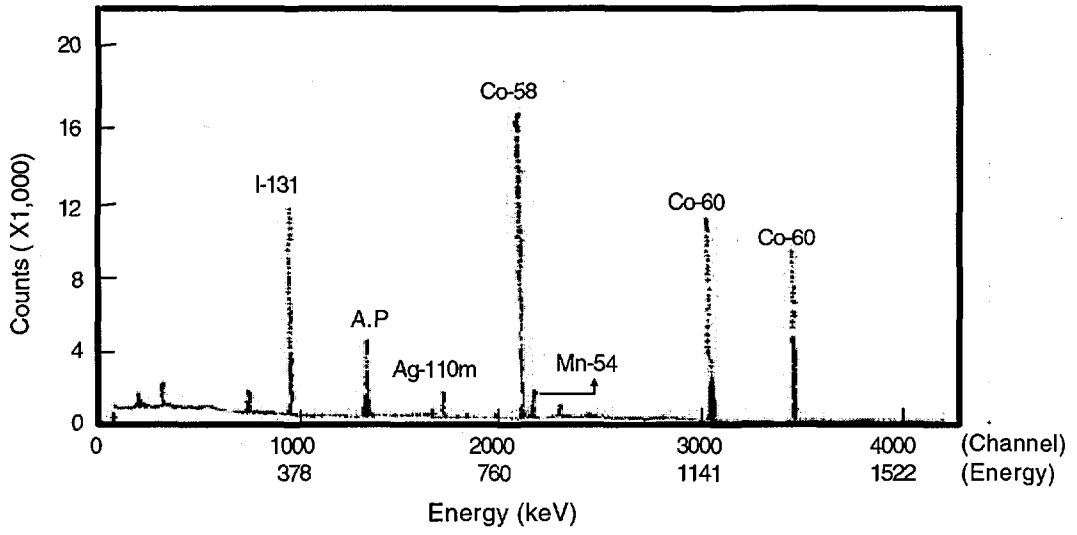

Figure 1. ¥ã-spectroscopy results of spent nuclear steam generator tube.

In the mean time, research on the etching of metallic conductor materials such as Ta, Mo, and Cu has been practically and actively carried out in the semi-conductor industry for the replacement of aluminum in order to meet the need of development of VLSI[15-18]. Now the metal surface processing using plasma gas has been also highlighted in the nuclear industry because this method can reduce the secondary waste drastically while maintaining the same level of the efficiency with current wet decontamination method[19]. Especially, Co is one of the principal contaminants in the spent parts or equipment such as valves and pipes made of stainless steel or inconel in the nuclear reactor. Fig.1 shows the gamma spectroscopic results of the inconel tube recently extracted from the spent steam generator of a domestic nuclear power plant, which demonstrates that the isotopes of Co are the major contaminants in the tube.

Therefore, another option may become available in the development of dry decontamination/surface-cleaning technology of the radioactive waste if this plasma etching technique is successful and effective. In this study, fundamental reaction studies are performed on the etching reaction of the three substances under investigation by using r.f. plasma with the etchant gas of CF_4/O_2 mixture.

EXPERIMENTALS

The apparatus for the etching reaction in CF_4/O_2 mixture gas plasma is designed and manufactured to meet the experimental purposes (Fig. 2). The plasma reactor is a diode type and r. f. power of up to 600W is applied between the parallel electrodes. The distance between them can be adjusted, however, it remains stationary (10 cm) during the current experiments. Samples can be heated up to 600¡É by the electrical heater inside the reaction chamber. Mass flow controllers fine-control the flow rates of CF_4 and O_2 that are mixed before they reach the reaction chamber. Total gas pressure is maintained around 0.45 Torr during experiments.

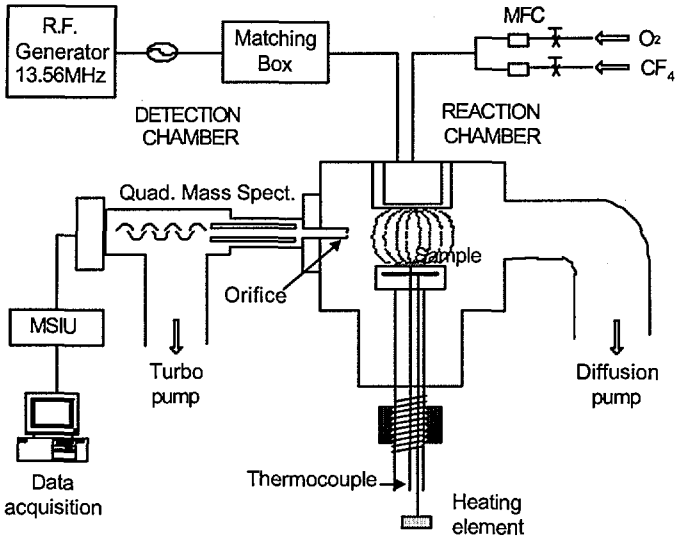

Figure 2. A schematic of plasma etching reaction apparatus

In the experiments thin disk type specimens are prepared using low speed diamond wheel cutter. Natural uranium dioxide cut out of a pellet is used for UO_2 experiment while non-radioactive metal samples with 99.8 % purity are used for metallic specimens. Prior to the sample loading, surface of the specimen is polished as mirror-like by grit 600 sandpaper, cleaned by ultrasonic cleaner, and baked at 200¡É for 10 minutes in a vacuum to evaporate adsorbed moisture on the surface.

First, etching reactions are examined with various CF_4/O_2 ratios to find the highest etching rate as a function of CF_4/O_2 ratio. Then, substrate temperature is varied at the optimum gas composition. Plasma power and exposure duration are the next experimental variables. OES (Optical Emission Spectroscopy) analysis is accompanied with the main experiments to determine the intensities of neutral radicals in the plasma while reactants and reaction products are *in-situ* detected and identified by a PC-controlled quadrupole mass spectrometer (model HAL-3F/PIC, Hiden Anal. Ltd.) sitting in the detection chamber.

Etching reaction rate is determined by weight loss measurement before and after the reaction with an electro-micro balance (BP210D, Sartorius) whose sensitivity limit is 10^{-5}g.

RESULTS AND DISCUSSION

RESULTS OF UO_2 REACTION

Under various r.f. power of up to 150W, etching reactions are examined with various CF_4/O_2 ratios for 100 minutes at several substrate temperatures. Some of the experimental results are plotted in Figs. 3 a) and b). These figures reveal that there exists an optimum CF_4/O_2 ratio for the efficient etching of UO_2 which is around 4 at the substrate temperature up to 370¡É, regardless of r.f. power and substrate temperature.

The highest etching rate at 370¡É under 150 W exceeds 1000 monolayers/min. which is equivalent to 0.4 ¥ìm/min. and comparable to that of the Si wafer in the semi-conductor industry.

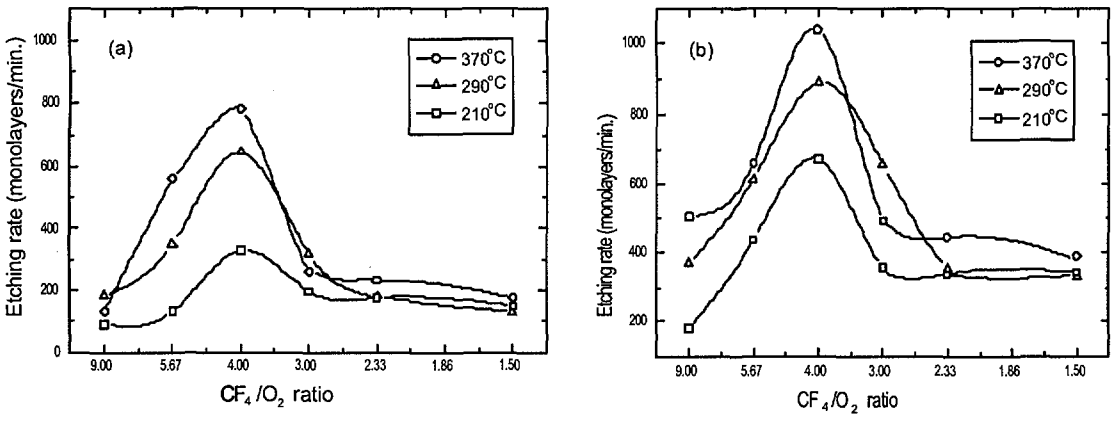

Figure 3. Reaction rate vs. O_2 mole fraction under r.f. power of (a) 100W and (b) 150W

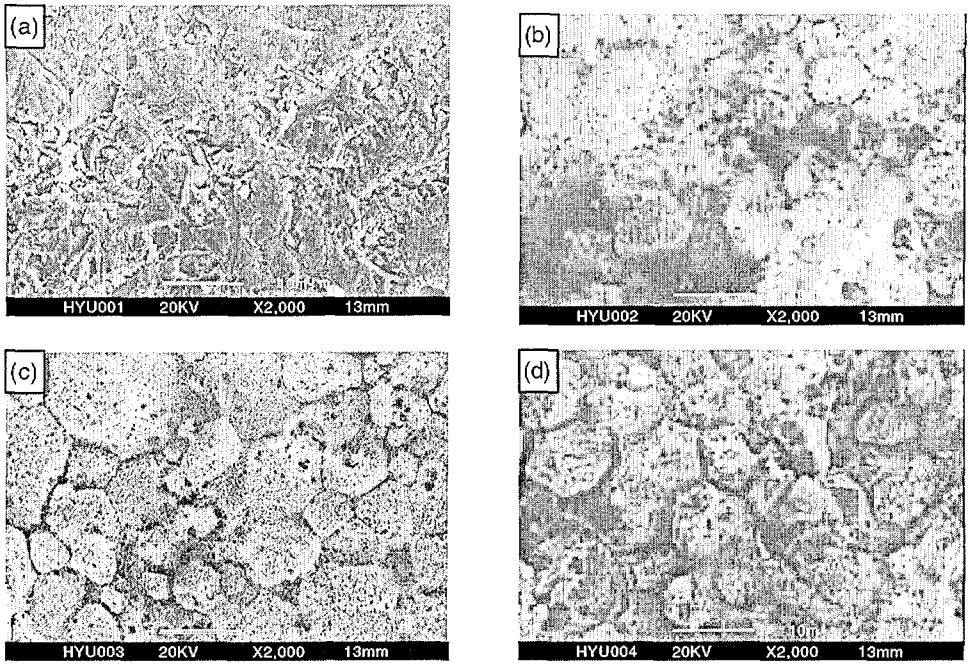

Figure 4. UO_2 surface morphologies by SEM (a) before reaction (b) 80%CF_4-20%O_2 (c) 90%CF_4-10%O_2 (d) 60%CF_4-40%O_2 plasma reaction

Surface morphology changes before and after the reaction in Fig. 4 support that only at the optimum gas composition the etching reaction vigorously takes place all over the surface, both on the grain surfaces and in the grain boundaries. It is found that at non-optimum gas composition carbon deposit accumulates or hyper-stoichiometric uranium oxide forms on the surface, respectively depending on the insufficiency or excessivity of oxygen, which retards the surface etching reaction[13,14].

In the previous work[14], it is reported that the major reaction product is uranium hexa-fluoride, UF_6, and thus the dominant overall reaction is determined: UO_2 + 3/2 CF_4 + 3/8 O_2 = UF_6 + 3/2 (CO or CO_2). XPS (X-ray Photoelectron Spectroscopy) confirmed the formation of UO_2F_2 on the surface, which reveals that critical reaction path is UO_2 ¡æUO_2F_2 ¡æUF_6 in the overall reaction. The reaction follows a linear kinetics, that is, surface-reaction rate-limiting with the activation energy of 12.1 kJ/mole which is comparable to 10.4 kJ/mole for Si and 15.8 kJ/mole for SiO_2. It is also found that the etching reaction rate at the optimum gas composition proportionally increases as substrate temperature and/or r. f. plasma power go up.

RESULTS OF METALLIC COBALT REACTION

Fig. 5a) shows the experimental results with various mole fractions of O_2 under 220 W r.f. power at 380¡É substrate temperature for 120 minutes. As shown in the figure, the highest reaction rate is achieved also at 20 % O_2 mole fraction. In order to examine the temperature dependency of the etching rate, substrate temperature is varied from 290¡É up to 380¡É under the same r.f. power, maintaining the optimum CF_4/O_2 ratio for 120 minutes. As seen in Fig. 5b), weight loss due to the

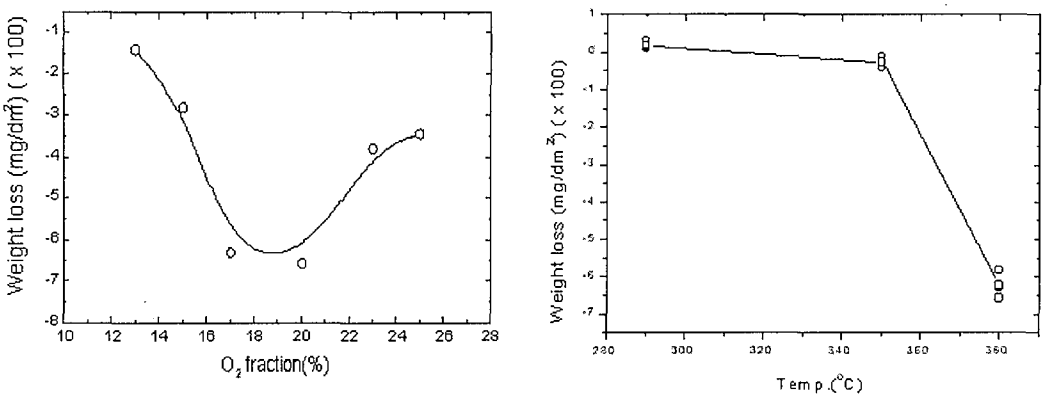

Figure 5 Co etching reaction rate under 220 W r.f. power (a) vs. O_2 mole fraction at 380¡É (b) vs. substrate temperature at 20 % O_2 mole fraction

surface reaction is hardly measured at 290¡É, but the etching reaction begins to take place at around 350¡É and the rate increases sufficiently as temperature goes up. Maximum etching rate achieved at 380¡É is 0.06 ¥ìm/min.

To support these results, the surface morphological change of the specimen is analyzed by using SEM. Fig. 6a) shows a mirror-like flat surface before the reaction and in Fig. 6b) very rough surface is observed after the reaction.

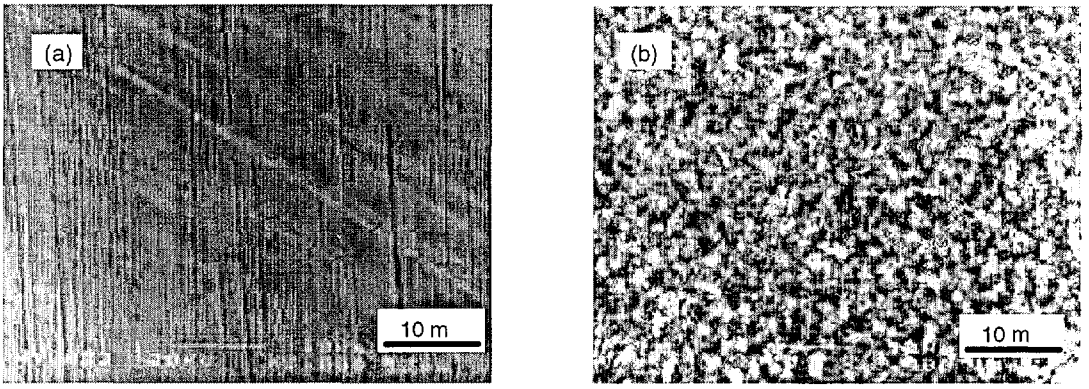

Figure 6 Co surface morphology by SEM (a) before reaction (b) after reaction with CF_4/O_2(20 %) gas plasma.

RESULTS OF METALLIC MOLYBDENUM REACTION

Similar experiments to those of Co is performed with varying the composition of the etchant gas. Fig. 7a) shows that, as in the cases of UO_2 and Co, the optimal mole fraction of O_2 is turned out to be 20 % for the efficient etching under r.f. power of 220 W. From the investigation of temperature dependency, it is found that the reaction rate is very high and the etching rate increases exponentially as temperature increases (Fig. 7b). The maximum etching rate, 1.9 ¥ìm/min, is obtained at 380¡É. This high reaction rate has not been expected because Mo is

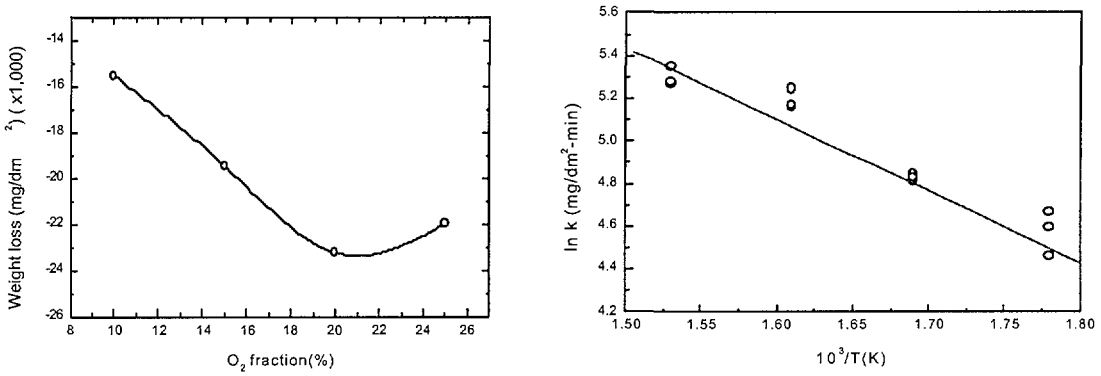

Figure 7. Mo etching reaction rate under 220W r.f. power (a) vs. O_2 mole fraction at 380¡É (b) vs. substrate temperature at 20 % O_2 mole fraction.

thermally and mechanically very stable (m.p.: 2,617¡É), thus, classified as a refractory metal. In this study, it is demonstrated that Mo can be chemically attacked very easily in certain environmental conditions.

SEM analysis on the surface morphology before and after the reaction demonstrates that vigorous reaction takes place on the whole surface (Fig. 8).

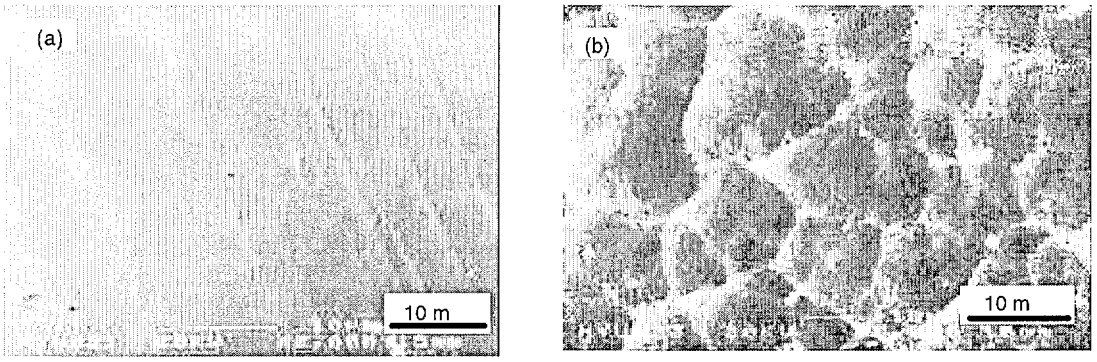

Figure 8. Mo surface morphology by SEM (a) before reaction (b) after reaction with CF_4/O_2(20 %) gas plasma.

OES (Optical Emission Spectroscopy) ANALYSIS

Plasma diagnosis by OES analysis is carried out to figure out the fundamental reaction mechanisms between the CF_4/O_2 plasma and three substances, UO_2, Co, and Mo, under investigation. Intensities of fluorine atom, oxygen atom, and CO molecule are examined as a function of O_2 mole fraction in the CF_4/O_2 plasma. Fig. 9 shows that intensities of F and CO reach maximum at 20 % mole fraction of O_2. This result basically supports that major reactions in the current investigation may be the fluorination reactions, taking their strong chemical affinities with fluorine atom/molecules into the consideration. In cases of Co and Mo, CO generated in plasma may take part in the reaction to form carbonyl compounds that have very low melting temperature and high vapor pressure. More fundamental studies on the reaction mechanisms will be carried out.

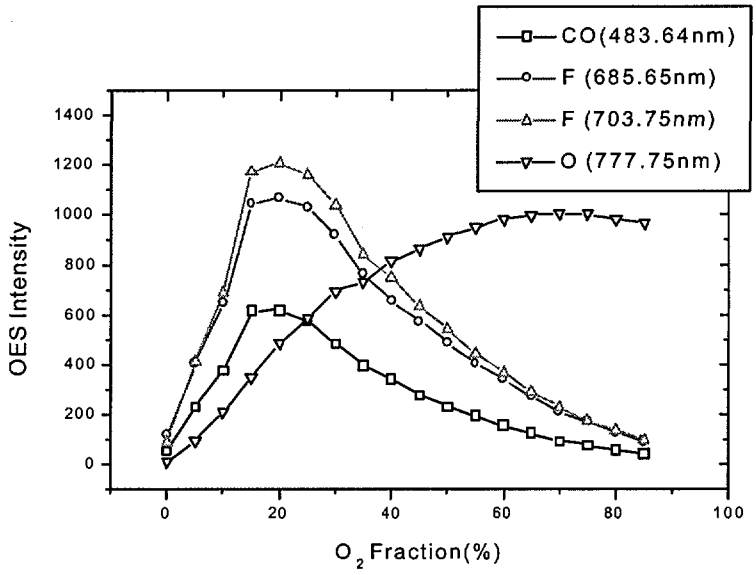

Figure 9. Emission intensities of F, O, and CO in the plasma as a function of O_2 mole fraction.

CONCLUSIONS

Experimental studies on the reaction between CF_4/O_2 plasma and UO_2, Co, and Mo, representing major contaminants in a nuclear power system, has been performed in order to demonstrate the feasibility and the applicability of dry decontamination technique using gaseous plasma.

Results show that in all cases maximum etching rate is achieved when the mole fraction of O_2 to CF_4/O_2 mixture gas is 20 %, regardless of temperature and r.f. power. In case of UO_2, the highest etching reaction rate is greater than 1000 monolayers/min. at 370¡É under 150 W r.f. power which is equivalent to 0.4 ¥ì m/min. and comparable to that of the Si wafer in the semi-conductor industry. As for Co, reaction hardly occurs up to 350¡É, but the etching reaction begins to take place significantly when exceeding the temperature. Maximum etching rate achieved at 380¡É is 0.06 ¥ì m/min. In the case of Mo, etching reaction takes place vigorously even at relatively low temperature and the reaction rate increases drastically with increasing temperature. Highest etching rate at 380¡É is 1.9 ¥ì m/min.

According to OES analysis, primary reaction seems to be a fluorination reaction, but carbonyl reaction may assist the dominant reaction, especially in case of Co and Mo.

Through this basic study, therefore, the feasibility and the applicability of plasma decontamination technique may be demonstrated. For example, in case that those nuclides are the major contaminants on the certain surface in the spent nuclear parts and equipment such as valves and pipes, simultaneous decontamination will be possible using CF_4/O_2 mixture gas plasma with other combinations of plasma parameters such as temperature and power.

Future works have been planned and thus more fundamental and practical studies will be carried out.

REFERENCES

[1] USAEC Report *ANL-5924* (1958)
[2] W.J. Mecham, J.D. Gabor, and A.A. Jonke, *Chem. Eng. Progr. Symp. Ser. 60*, **47** (1964) 76.
[3] A.A. Jonke, *Atomic Energy Rev.*, **3** (1965) 3.
[4] L.J. Anastasia and W.J. Mecham, *I & EC Process Design Devel.*, **4** (1965) 338.
[5] T. Yahata and M. Iwasaki, *J. Inorg. Nucl. Chem.*, **26** (1964) 1863.
[6] G. Vandenbussche, *CEA-R 2859* (1966)
[7] M. Iwasaki, *J. Nucl. Mater.*, **25** (1968) 216.
[8] J.C. Batty and R.E. Stickney, *J. Chem. Phys.*, **51** (1969) 4475.
[9] B. Weber and A. Cassuto, *Surf. Sci.*, **39** (1973) 83.
[10] A.J. Machiels and D.R. Olander, *High Temp. Sci.*, **9** (1977) 3 .
[11] H. Keil, P. Boczar, and H.S. Park, *Proc. Intern. Conf. Tech. Expo. on Future Nuclear Systems, Global '93,* Seattle, Washington, USA (Sept. 12-17, 1993) 733.
[12] M.S. Yang, Y.W. Lee, K.K. Bae, and S.H. Na, *Proc. Intern. Conf. Tech. Expo. on Future Nuclear Systems, Global '93*, Seattle, Washington, USA (Sept. 12-17, 1993) 740.
[13] Y. Kim, J. Min, K. Bae, M. Yang, J. Lee, and H. Park, *Proc. Intern. Conf. On Future Nuclear Systems, Global '97*, Yokohama, Japan (Oct. 5-10, 1997) 1148.
[14] Y.S. Kim, J.Y. Min, K.K. Bae, and M.S. Yang, *J. Nuclear Mater.*, **270** (1999) 253.
[15] J. C. Martz, D. W. Hess, and W. E. Anderson, *J. Appl. Phys.*, 67 (1990) 3609.
[16] Y. Igarashi, T. Yamanobe, and T. Ito, *J. Electrochem. Soc.*, 142 (1995) L36.
[17] J. W. Lee, Y. D. Park, J. R. Childress, S. J. Pearton, F. Sharifi, and F. Ren, *J. Electrochem. Soc.*, **145** (1998) 2585.
[18] Y. Kuo and S. Lee, *Jpn. J. Appl. Phys.*, **39** (2000) L188.
[19] J. J. Barghusen, A. A. Jonke, N. M. Levitz, M. J. Steindler, and R. C. Vogel, Fluid-Bed Fluoride Volatility Processing of Spent Fuel Reactor Materials, Progress in Nuclear Energy, Series III, Vol. 4, *Process Chemistry*, C. E. Stevenson, E. A. Mason, A. T. Gresky (eds.), Pergamon Press, (1970) 347.