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A Study on Etching of UO_2, Co, and Mo Surface with R.F. Plasma Using CF_4 and O_2

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Abstract

Recently dry decontamination/surface-cleaning technology using plasma etching has been focused in the nuclear industry. In this study, the applicability 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 while metallic Co and Mo are selected because they are the principal contaminants in the used metallic 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 in 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°C under 150 W r.f. power which is equivalent to 0.4 μm/min. As for Co, etching reaction begins to take place significantly when the temperature exceeds 350°C. Maximum etching rate achieved at 380°C is 0.06 μm/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°C is 1.9 μm /min.

According to OES (Optical Emission Spectroscopy) and AES (Auger Electron Spectroscopy) analysis, primary reaction seems to be a fluorination reaction, but carbonyl compound formation 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 are demonstrated.

Key Words : decontamination, radwaste, plasma processing

1. 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, 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 of the new dry plasma 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 processe is 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 compound 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 gaseous plasma with fluorine was proposed and its applicability has been demonstrated[13,14].

In the mean time, research on the etching of metallic conductor materials such as Ta, Mo, and Cu has been actively carried out in the semiconductor 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 used parts or equipment such as valves and pipes made of stainless steel or inconel in the nuclear reactor. Fig.1 shows the gamma spectrum of the inconel tube recently extracted from the used steam generator of a domestic nuclear power plant, which demonstrates that the isotopes of Co are the major contaminants in the tube.

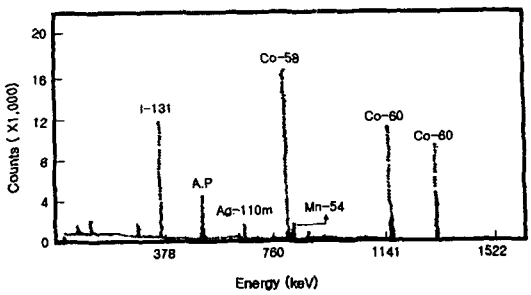


Fig. 1. γ-spectrum Results of Used Nuclear Steam Generator Tube

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 studies of the plasma etching reaction of the three elements are performed using r.f. plasma with the etchant gas of CF_4/O_2 mixture.

2. Experimentals

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

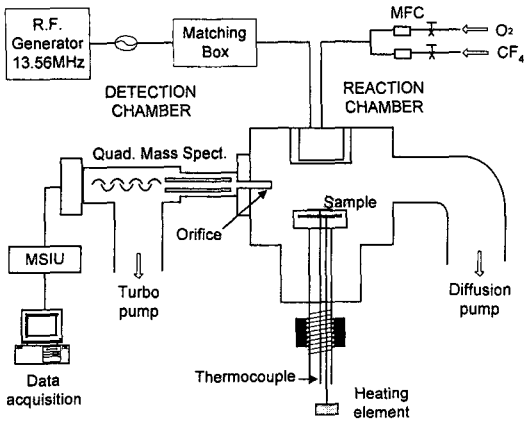


Fig. 2. A schematic of Plasma Etching Reaction Apparatus

plasma reactor is a diode type and r. f. power of up to 600W is applied between the parallel electrodes. Though the distance between them can be adjusted, it remains stationary (10 cm) during the current experiments. Samples can be heated up to 600℃ by the electrical heater inside the reaction chamber. The flow rates of CF_4 and O_2 sre finely adjusted by the mass flow controllers and the gases are mixed before the supply to the reaction chamber. Total gas pressure is maintained around 0.45 Torr during the experiments.

Thin disk type specimens are prepared for the experiments 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 elements experiments. 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℃ 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.

3. Results and Discussion

3.1. Results of UO_2 Reaction

Under various r.f. power 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 and it is about four at the substrate temperature up to 370℃, regardless of r.f. power

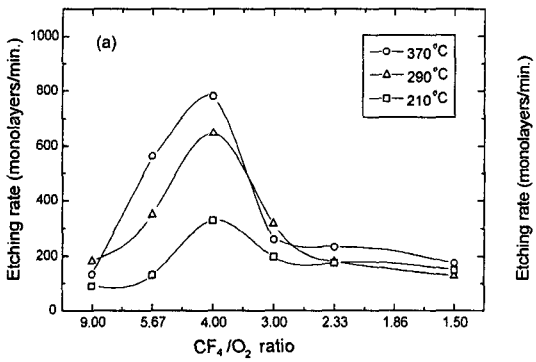


Fig. 3. Reaction Rate vs. O_2 Mole Fraction Under r.f. Power of (a) 100W and (b) 150W

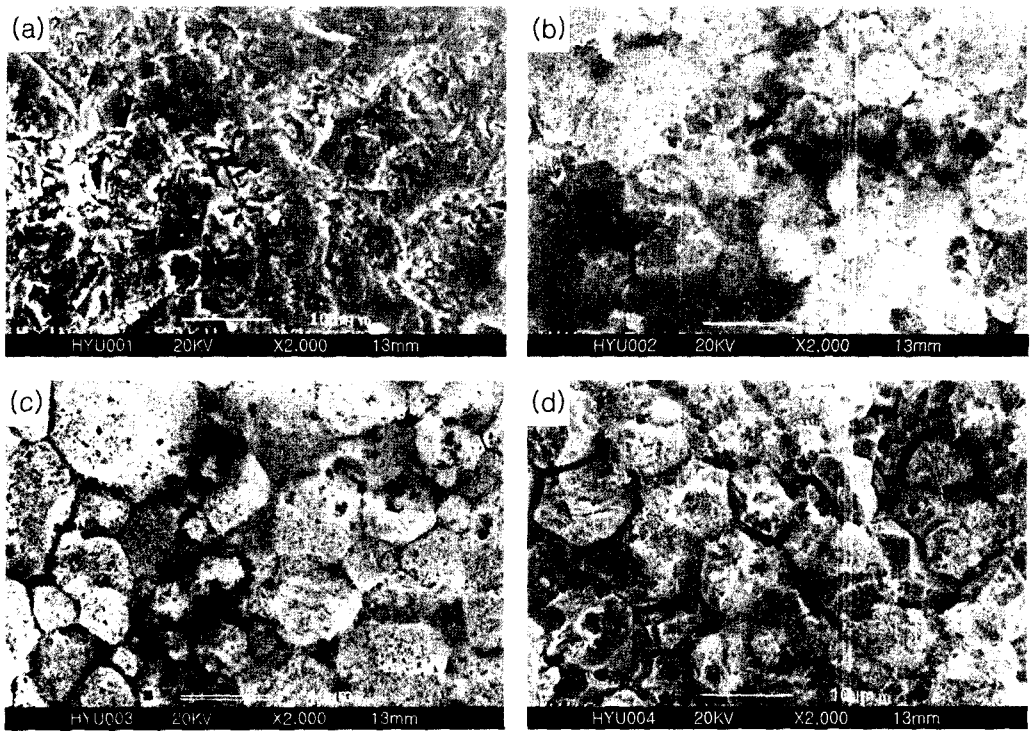


Fig. 4. UO_2 Surface Morphologies by SEM (a) Before Reaction (b) 80%CF_4-20%O_2 (c) 90%CF_4-10%O_2 (d) 60%CF_4-40%O_2 Plasma Reaction

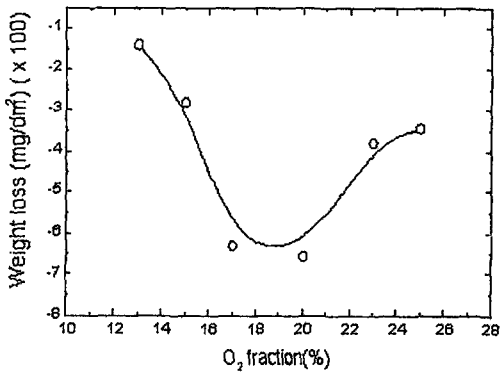
and substrate temperature. The highest etching rate at 370℃ under 150 W exceeds 1000 monolayers/min. which is equivalent to 0.4㎛/min. and comparable to that of the Si wafer in the semi-conductor industry.

Surface morphology changes before and after the reaction as shown 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 depending on the insufficiency or excess of oxygen, respectively. These processes retard the surface etching reaction[13,14].

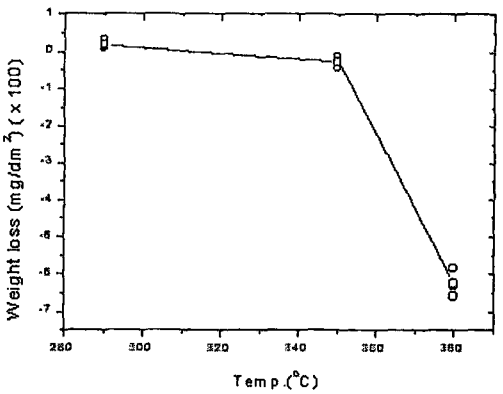
In the previous work[14], it is reported that the major reaction product is uranium hexa-fluoride, UF_6, and the dominant reaction is $UO_2 + 3/2\ CF_4 + 3/8\ O_2 = UF_6 + 3/2$ (CO or CO_2). XPS (X-ray Photoelectron Spectroscopy) confirmed the formation of UO_2F_2 on the surface and it reveals that critical reaction path is $UO_2 \rightarrow UO_2F_2 \rightarrow UF_6$ in the overall reaction. The reaction follows a linear kinetics, that is, surface-reaction is 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 r.f. plasma power go up.

3.2. Results of Metallic Cobalt Reaction

Fig. 5 a) shows the experimental results of metallic cobalt with various mole fractions of O_2



(a) Etching Rate vs. O_2 Mole Fraction at 380 ℃



(b) Etching Rate vs. Substrate Temperature at 20% O_2 Mole Fraction

Fig. 5. Co Etching Reaction Rate Under 220 W r.f. Power

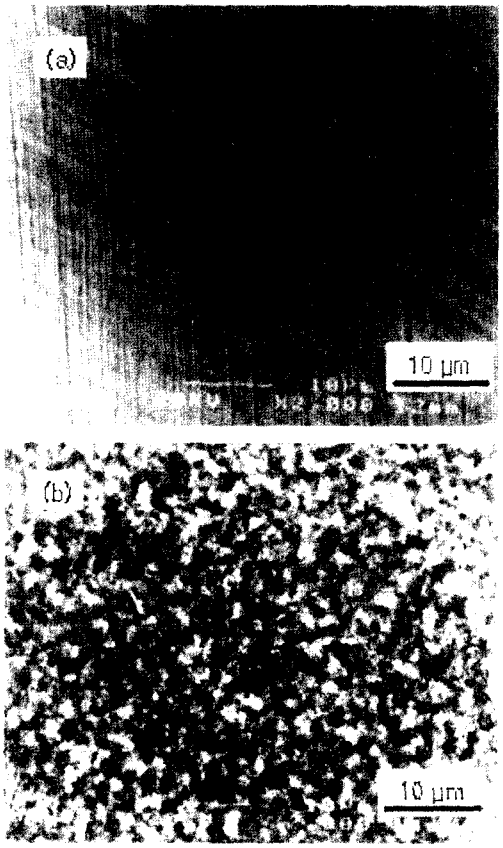


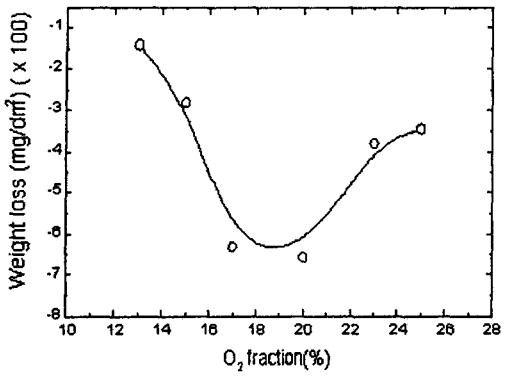
Fig. 6. Co Surface Morphology by SEM (a) Before Teaction (b) After Reaction with CF_4/O_2(20 %) Gas Plasma

under 220 W r.f. power at 380℃ 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℃ up to 380℃ 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 surface reaction is hardly measured at 290℃, but the etching reaction begins to take place at around 350℃ and the rate increases sufficiently as temperature goes up. Maximum etching rate achieved at 380℃ is 0.06 μm/min.

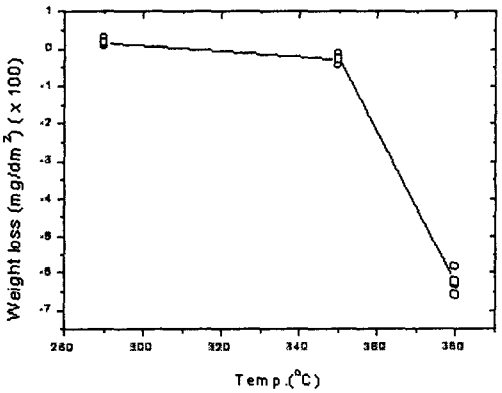
To support these results, the surface morphological change of the specimen is analyzed by using SEM. Fig. 6a) shows a mirror-like flat surface before the reaction and very rough surface is observed after the reaction in Fig. 6b).

3.3. Results of Metallic Molybdenum Reaction

Surface etching reaction is investigated with varying the composition of the etchant gas. Fig.



(a) Etching Rate vs. O_2 Mole Fraction at 380℃



(b) Etching Rate vs. Substrate Temperature at 20% O_2 Mole Fraction

Fig. 7. Mo Etching Reaction Rate Under 220W r.f. Power

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 temperature dependency investigation, 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 (m/min, is obtained at 380℃. This high reaction rate has not been expected because Mo is thermally and mechanically very stable (m.p.: 2,617℃), thus,

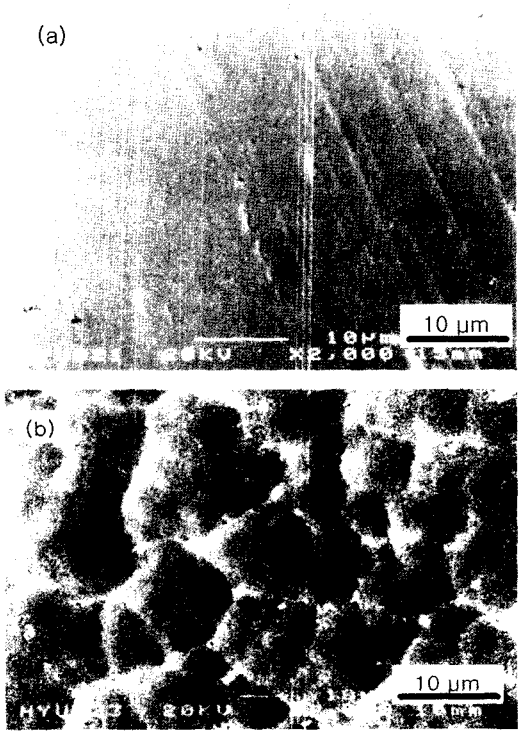


Fig. 8. Mo Surface Morphology by SEM (a) Before Reaction (b) After Reaction with CF_4/O_2(20 %) Gas Plasma

classified as a refractory metal. But, this study demonstrates that Mo can be chemically attacked very easily in certain environmental conditions.

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

3.4. OES and AES Analysis

Plasma diagnosis by OES (Optical Emission Spectroscopy) analysis is carried out to figure out the fundamental reaction mechanisms between the CF_4/O_2 plasma and three substances, UO_2, metallic Co, and metallic 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

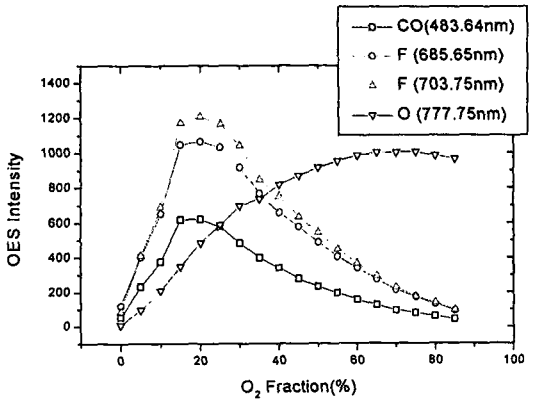
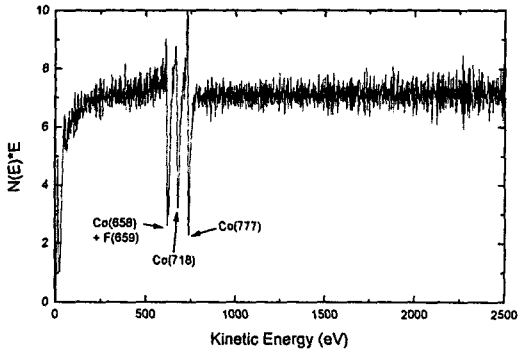
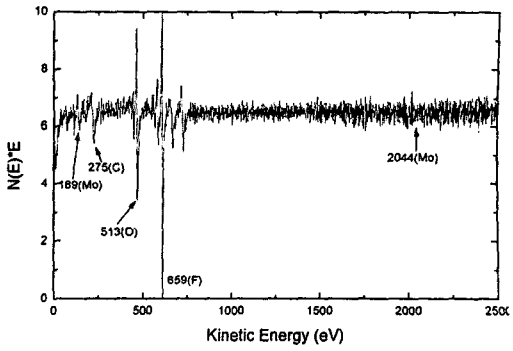


Fig. 9. Emission Intensities of F, O, and CO in the Plasma as a Function of O_2 Mole Fraction



(a) AES Peaks on the Reacted Co Surface (F (659) Peak is Hidden by Co (658))



(b) AES Peaks on the Reacted Mo Surface

Fig. 10. Surface Elements Analysis Results with AES

intensities of F and CO reach the maximum values at 20 % mole fraction of O_2. This result basically supports that major reactions in the current investigation seem to be the fluorination reactions, considering their strong chemical affinities with fluorine atom/molecules.

For the identification of reaction products in the Co and Mo surface reactions, surface atom concentrations are examined after the reaction by using AES (Auger Electron Spectroscopy) analysis. As seen in Fig. 10, fluorine atoms are detected on the reacted surfaces of the both specimens. This strongly supports that the surface etching reaction are mainly the fluorination reactions. In these cases, however, CO generated in plasma may take part in the reaction to form carbonyl compounds that have very low melting temperature and high vapor pressure.

4. Conclusions

Experimental studies on the reaction of UO_2, Co, and Mo with CF_4/O_2 plasma, representing major contaminants in a nuclear power system, have 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 in the 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℃ under 150 W r.f. power which is equivalent to 0.4 μm/min. and comparable to that of the Si wafer in the semiconductor industry. As for Co, reaction hardly occurs up to 350℃, but the etching reaction begins to take place significantly when exceeding

the temperature. Maximum etching rate achieved at 380℃ is 0.06 μm/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℃ is 1.9μm/min.

According to OES and AES analyses, 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 is demonstrated. For example, in case that those nuclides are the major contaminants on the certain surface in the used nuclear parts or equipment such as valves and pipes, simultaneous decontamination will be effectively carried out using CF_4/O_2 mixture gas plasma with other combinations of plasma parameters such as temperature and plasma power.

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