

Reaction of Uranium Dioxide with CF₄/O₂ r. f. Plasma

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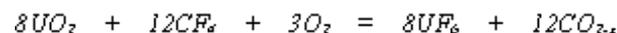
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Abstract

Research on the etching reaction of UO₂ in CF₄/O₂ r. f. plasma is carried out at temperatures of up to 370°C under the total pressure of 0.3 Torr. The reaction rates are investigated as functions of CF₄/O₂ ratio, plasma power, and substrate temperature. It is found that the highest etching rate is obtained at 20%O₂ mole fraction regardless of r. f. power and substrate temperature. The highest etching reaction rate at 370°C under 150W exceeds 1000 monolayers/min, which is equivalent to 0.4 μm/min. The mass spectrometry analysis result reveals that the major reaction product is uranium hexa-fluoride UF₆. Based on the experimental findings, dominant overall reaction of uranium dioxide in CF₄/O₂ plasma is determined:



where CO_{2x} represents the undetermined mix of CO₂ and CO.

1. Introduction

Recently the feasibility of burning spent PWR fuel in a CANDU reactor was

carried out. In the proposed process decladding of spent fuel pins and dry-processing of burned UO_2 such as OREOX (Oxidation and REduction of OXide fuel) process are the main processes to make re-sinterable fuel powder [1,2]. Most candidate mechanical decladding techniques were unable to recover more than 98 to 99.5% of the heavy metal/metal oxide. Thus, a plasma processing technique using fluorine containing gas plasma is proposed as a secondary decontamination process and its applicability is demonstrated [3]. For current research, the reaction rates of UO_2 in CF_4/O_2 r. f. plasma are determined and the overall reaction mechanism is investigated in detail.

The fluorination of UO_2 has been extensively studied in the application-oriented fields such as uranium separation, processing, and conversion [4,5]. Along with the applied research, fundamental studies of the UO_2/F_2 reaction have been reported by several authors [6-10].

The reaction of UO_2 at low temperatures (below 800K) under atmospheric pressure of F_2 was studied using weight loss measurements by Vandebussche [6] and by Iwasaki [7]. Under these conditions the ultimate reaction products are found to be UF_6 and O_2 , while a variety of intermediate reaction products such as $(\text{UO}_2)_4\text{F}$ and UO_2F_2 are identified. On the contrary, a quasi-equilibrium reaction modelling study predicted that at high temperatures (above 1000K) under low pressure of F_2 ($10^{-7} \sim 10^{-4}$ Torr), UF_5 and UF_6 formations are suppressed in favor of UF_4 and atomic fluorine formation [8,9]. A kinetic study carried out later at high temperatures (above 1000K) under ultra-high vacuum condition confirmed that the reaction product is UF_4 and the reaction probability is about 10^{-2} [10]. The authors claimed that the reaction mechanism is a second-order surface reaction coupled with the double-diffusion process. The disagreement between these early experimental results seems to stem from the different ranges of temperatures and pressures. Thus, the extrapolation of the results in one range to another must be carefully made even in cases of necessity.

2. Experimental

The apparatus for UO_2 etching reaction with CF_4/O_2 r. f. plasma is designed and manufactured to meet the experimental purposes (Fig. 1). 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 up to 10 cm. However, it remained

stationary during the current experiments. The heating element in the reaction chamber can heat samples, mostly thin disk or wafer-like samples of maximum 10 cm in dia, up to 800°C. Mass flow controllers fine-control the flow rates of CF₄ and O₂ gas and total gas pressure is varied using the main throttle valve.

In the experiments thin disks (0.35 mm in thickness) of natural uranium dioxide cut out of a pellet are used as specimens. Prior to the sample loading, specimens are polished by grit 600 sandpaper, cleaned by ultrasonic cleaner, and baked at 200°C for 10 minutes in a ultra-high vacuum to evaporate the adsorbed moisture on the surface.

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 10⁻⁵g. Reactants and generation of reaction products are *in-situ* detected by the quadrupole mass spectrometer (model HAL511, Hiden Anal. Ltd.) sitting in the detection chamber and identified by a PC-controlled data acquisition system.

3. Results and Discussion

In the experiments total gas pressure is maintained at 0.3 Torr while CF₄/O₂ ratio is varied and r. f. plasma power of up to only 150W is applied because of temperature control difficulties resulting from internal heating of the chamber.

First, under r. f. power of 100W and 150W, etching reactions are examined with various CF₄/O₂ ratios for 100 minutes at several substrate temperatures of up to 370°C. The etching rate is estimated using the following formula:

$$\frac{1}{(\rho N_a/M)^{2/3}} \frac{\Delta W}{At} \frac{N_a}{M} \text{ (monolayers/min)}$$

where ρ is UO₂ density (10.96 g/cm³), N_a is Avogadro's number, M is UO₂ atomic mass (270.03 g/mole), ΔW is weight loss due to etching reaction, A is area of the sample, and t is duration of exposure to plasma.

The experimental results are plotted in Fig. 2 a) and b). The figures reveal that there exists an optimum CF₄/O₂ ratio for the reaction regardless of r. f. power, plasma geometry, and substrate temperature and that it is around 4:1 under the substrate temperature of 370°C. In actuality, under 100 W r. f. power, the optimum

composition is additionally examined at different plasma geometries with finely-varied gas composition (closed symbol data in Fig. 2 a). Reaction rate peaks are vividly observed at all temperature under 370 °C and they increase with increasing temperature. The highest etching reaction rate at 370 °C under 150W exceeds 1000 monolayers/min., which is equivalent to 0.4 μm/min. and comparable to that of the Si wafer in the semi-conductor industry.

In the fluorination of UO₂ to UF₆ with fluorine, the formation of UO₂F₂ on the surface as a primary intermediate has already been reported [7,11]. For the identification of this species, the surface elements of reacted and unreacted specimens are analyzed by XPS (X-ray Photoelectron Spectroscopy) and their peaks over a binding energy spectrum are shown in Fig. 3 a). The fluorine peaks re-plotted in detail in Fig. 3 b) shows that the intact UO₂ specimen has no fluorine on the surface. On the other hand, the reacted surface is covered with the compounds of uranium, oxygen, and fluorine, which confirms that fluorine compounds, possibly UO₂F₂, form on the surface.

Carbon peaks are also re-plotted in detail in Fig. 3 c). During the experiment, oxygen gas is injected in the feed gas to pick up and remove the carbon atoms by forming volatile species such CO or CO₂, since it is fundamentally believed that carbon residuals decomposed from CF₄ may deposit on the surface and suppress surface reaction. Thus, it is supposed that at oxygen gas compositions of lower than the optimum, the amount of oxygen (molecule or atom) is not enough to pick up the carbon residuals. Hence, the surface carbon concentration is greater than that of the optimally reacted surface. This claim is supported by XPS analysis in the figure showing that the concentration is much lower than that of the non-optimum composition (10% O₂). On the other hand, at higher oxygen gas compositions, high reactivity of excessive oxygen with surface uranium atom may form hyper-stoichiometric uranium oxides instead of CO or CO₂ and interfere with the formation of volatile uranium fluorides. This postulation is partially demonstrated by XRD (X-ray Diffractometry) analysis in Fig. 4. Compared to X-ray diffraction patterns of uranium dioxide reacted in 20%O₂/80%CF₄ plasma, new peaks of uranium compounds such as U₄O₉, U₃O₇, and U₃O₈ are seen in the specimen reacted in 40%O₂/60%CF₄ plasma.

Reactants and generation of reaction products are *in-situ* identified by the quadrupole mass spectrometer in the detection chamber. Typical examples of detected

species over the mass spectrum are shown in Fig. 5 a) and b). The first figure shows that a lot of stable or meta-stable compounds containing fluorine such as COF_2 , COF , F_2 and F are produced in CF_4/O_2 plasma, which is in good agreement to the previous results [12]. From the elementary reaction point of view, therefore, the molecular and/or atomic fluorine produced in the plasma or dissociated from the intermediate species are believed to take part in the fluorination reaction of UO_2 . As expected, Fig. 5 b) reveals that several uranium fluorides are produced in the reaction, and apparently, UF_5 seems to be the most abundant species among the reaction products. However, according to the thermodynamic instability of UF_5 and characteristic fragmentation pattern of UF_6 (0.004 UF_6^+ , 1.00 UF_5^+ , 0.262 UF_4^+ , 0.283 UF_3^+ , 0.332 UF_2^+ [13]), it is concluded that the major reaction product is uranium hexa-fluoride, UF_6 and the minor species such as UF_4 and UF_5 are probably generated parasitically.

Based on the finding that there exists an optimum gas composition in this fluorination reaction and that the major reaction product is UF_6 , the dominant overall reaction of UO_2 in CF_4/O_2 plasma is determined:



where CO_{2-x} represents the undetermined mix of CO_2 and CO .

4. Conclusions

From the current investigation it is found that there exists an optimum CF_4/O_2 ratio for the efficient etching of UO_2 in CF_4/O_2 plasma regardless of r. f. power, plasma geometry, and substrate temperature, and that it is around 4:1 under the substrate temperature of 370°C . This optimum gas composition is explained by the experimental findings that, at oxygen gas compositions of lower than the optimum, the amount of oxygen is not enough to pick up the carbon residuals. Hence, the residuals decomposed from CF_4 may deposit on the surface and suppress surface reaction, while at higher oxygen gas compositions, high reactivity of excessive oxygen with a surface uranium atom may form hyper-stoichiometric uranium oxides instead of CO or CO_2 and interfere with the formation of volatile uranium fluorides.

The highest etching reaction rate at 370°C under 150W exceeds 1000 monolayers/min., which is equivalent to $0.4\ \mu\text{m}/\text{min}$. and comparable to that of the Si wafer in the semi-conductor industry.

According to the mass spectrometry, it is revealed that the major reaction product is uranium hexa-fluoride UF₆. Some minor species such as UF₄ and UF₅ are probably generated parasitically. Therefore, based on the experimental results the dominant overall reaction of uranium dioxide in CF₄/O₂ plasma is determined:



where CO_{2-x} represents the undetermined mix of CO₂ and CO.

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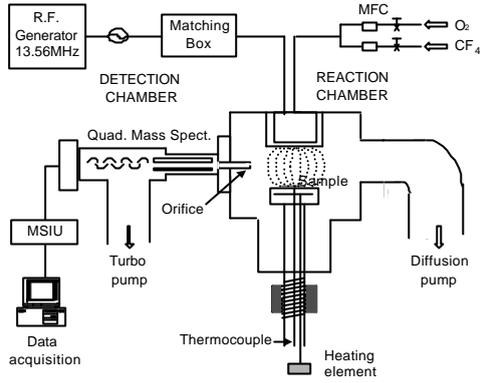


Fig. 1 A schematic of plasma etching reaction apparatus

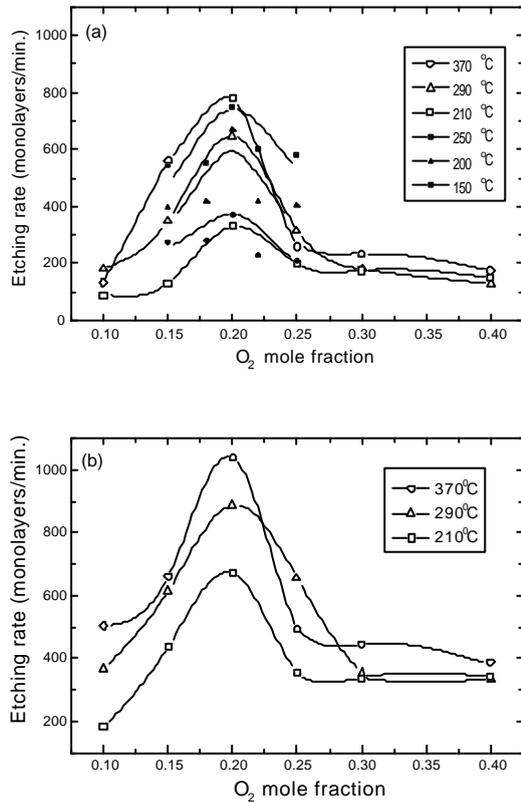


Fig. 2 Etching reaction rate vs. O_2 mole fraction
(a) 100W r.f. plasma (b) 150W r.f. plasma

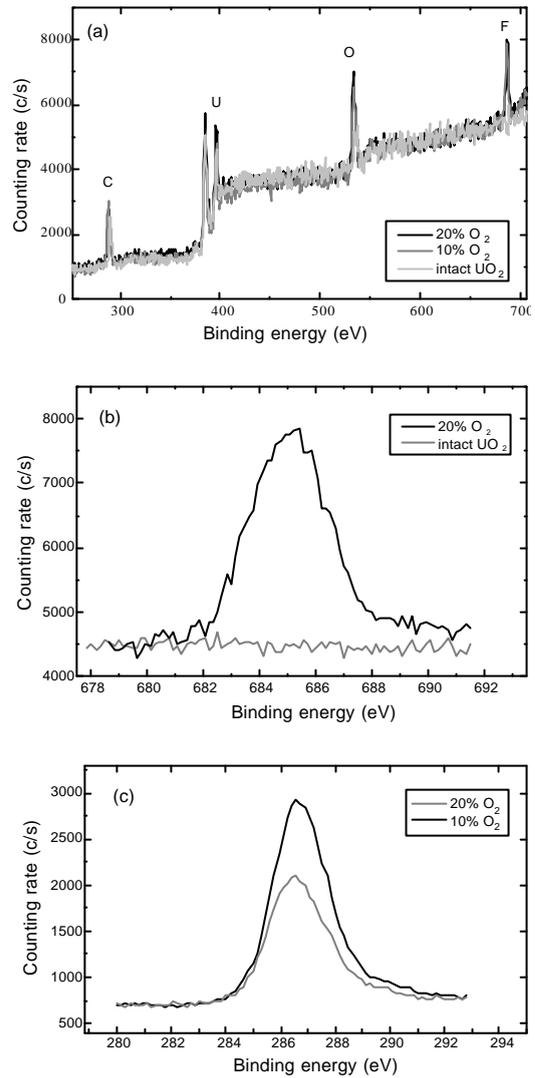


Fig. 3 (a) XPS spectrum of UO_2 after plasma etching, (b) fluorine and (c) carbon peaks in detail relative intensity to uranium peak intensity (total flow rate ; 50sccm, r.f. power ; 100W, substrate temperature ; 210°C, reaction time ; 100min.)

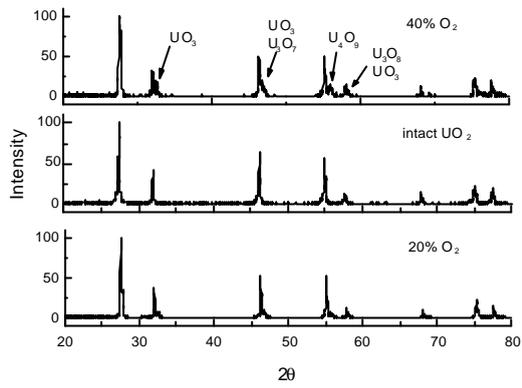


Fig. 4 XRD patterns of UO_2 specimen before and after reaction

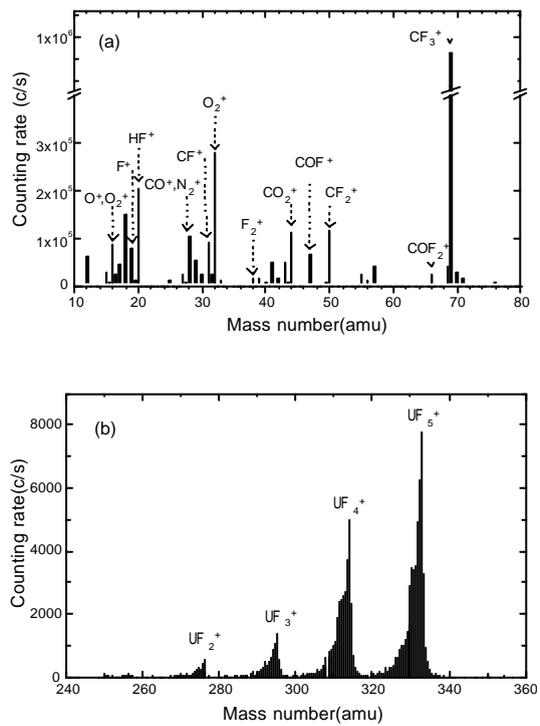


Fig. 5 (a) Reactants discharged in CF_4/O_2 plasma and (b) reaction products of UO_2 in CF_4/O_2 plasma