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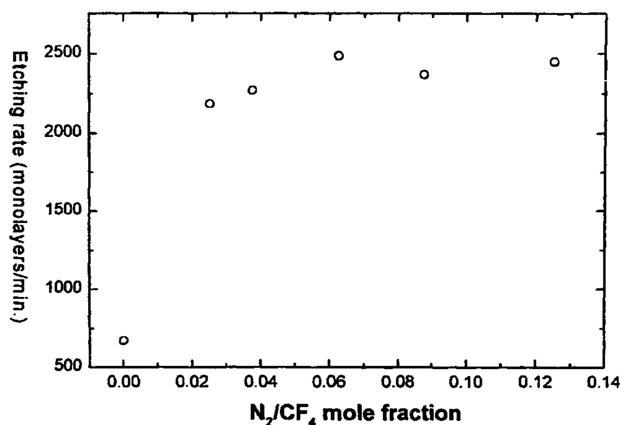
(54) Title: AN EFFECTIVE DRY ETCHING PROCESS OF ACTINIDE OXIDES AND THEIR MIXED OXIDES IN $CF_4/O_2/N_2$ PLASMA



UO_2 etching reaction rate vs. N_2/CF_4 mole fraction with the maintenance of the optimum CF_4/O_2 ratio at 290℃

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(57) Abstract: A process for gas-phase etching of actinide oxides from a substrate by using plasma power comprising the steps of: a) preheating actinide oxides on the substrate within a process chamber filled with fluorine-containing gas and exposing it to plasma power, and subsequently b) etching actinide oxides from the substrate using a plasma gas-phase reactant system.

AN EFFECTIVE DRY ETCHING PROCESS OF ACTINIDE OXIDES AND THEIR MIXED OXIDES IN $CF_4/O_2/N_2$ PLASMA

Technical Field

5 This invention relates to an effective dry etching process of actinide oxides and their mixed oxides in $CF_4/O_2/N_2$ PLASMA.

BACKGROUND OF THE INVENTION

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

15 [T. Yahata and M. Iwasaki, *J. Inorg. Nucl. Chem.*, **26** (1964) 1863, G. Vandenbussche, *CEA-R 2859* (1966), M. Iwasaki, *J. Nucl. Mater.*, **25** (1968) 216, J.C. Batty and R.E. Stickney, *J. Chem. Phys.*, **51** (1969) 4475, B. Weber and A. Cassuto, *Surf. Sci.*, **39** (1973) 83, A.J. Machiels and D.R. Olander, *High Temp. Sci.*, **9** (1977) 3].

20 The reaction of UO_2 at low temperatures of below 800K

under atmospheric pressure of F_2 was studied using weight loss measurements by Vandenbussche [G. Vandenbussche, *CEA-R 2859* (1966)] and by Iwasaki [M. Iwasaki, *J. Nucl. Mater.*, **25** (1968) 216]. 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 $(UO_2)_4F$ and UO_2F_2 are identified. On the contrary, a quasi-equilibrium reaction modelling study predicted that at high temperatures of above 1000K under low pressure of F_2 ($10^{-7} \sim 10^{-4}$ Torr), uranium hexa- and penta-fluoride formations are suppressed in favor of UF_4 and atomic fluorine formation [J.C. Batty and R.E. Stickney, *J. Chem. Phys.*, **51** (1969) 4475, and B. Weber and A. Cassuto, *Surf. Sci.*, **39** (1973) 83]

A kinetic study carried out later at high temperatures of above 1000 K under ultra-high vacuum condition confirmed that the reaction product is UF_4 and the reaction probability is about 10^{-2} [A.J. Machiels and D.R. Olander, *High Temp. Sci.*, **9** (1977) 3]. 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.

Recently the feasibility of burning spent PWR fuel in
5 a CANDU reactor was carried out, in which decladding of spent fuel pins and dry-processing of burned uranium dioxide such as OREOX (Oxidation and Reduction of Oxide fuel) process are the main processes to make re-sinterable fuel powder [H. Keil, P. Boczar, and H.S. Park, *Proc. Intern. Conf. Tech.*
10 *Expo. on Future Nuclear Systems, Global '93,* Seattle, Washington, USA [Sept. 12-17, 1993) 733 and 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]. In the process, however, most candidate decladding techniques were unable
15 to recover more than 98 to 99.5% of the heavy metal/metal oxide. A part of the remainder will be present as adherent dust and some may also be chemically bonded to the zirconium oxide layer on the inside of the fuel pin. Therefore, another process for additional removal of the
20 last portion of the fuel is required, which also removes

alpha contamination from the clad to a level qualifying the fuel hulls as non-TRU. For the secondary decontamination process, a plasma processing technique using fluorine-containing gas plasma was proposed and its applicability has been demonstrated [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]. Since then, dry etching treatments of TRU oxide including uranium dioxide have been extensively focused.

Following the demonstration, as a representative compound of actinide oxides including TRU dioxides, the effective etching reaction process of uranium dioxide in $CF_4/O_2/N_2$ plasma and reaction mechanisms have been investigated in detail in this work.

SUMMARY OF THE INVENTION

It is invented that the fluorination etching reaction of actinide oxides such as UO_2, ThO_2, and PuO_2 in CF_4/O_2 gas plasma is enhanced when small amount of N_2 gas is added or mixed at the temperature of ambience up to 600℃ under the

low pressure of 1 m Torr up to 1 atm. As a representing actinide, oxide uranium dioxide was chosen and its reaction rates were investigated as functions of $CF_4/O_2/N_2$ ratio, plasma power, substrate temperature, and exposure
5 time to the plasma. From the current investigation, it is found that there exists an optimum CF_4/O_2 ratio for the effective etching in $CF_4/O_2/N_2$ plasma. The ratio of CF_4 to O_2 is around four, regardless of plasma power, substrate temperature, and gas volume flow rate. When the small
10 amount of N_2 gas ranging from 1% to 20% of CF_4 gas based on the gas volume is added to or mixed with the optimized CF_4/O_2 the etching rate is enhanced remarkably over 4 up to 5 times compared to that of CF_4/O_2 plasma without N_2 gas.

This optimum etching process must be applicable to the
15 dry etching of other actinide oxides including TRU (TRans-Uranium) oxides and their mixed oxides since all actinide elements have very similar chemical characteristics with uranium and, thus, form similar types of oxides.

20 In current examination, r.f. and microwave power gas

plasma generation techniques were used with the power ranging 50W up to 2kW and the effectiveness of this process was confirmed. Since basic principle of gas plasma generation techniques is identical except different
5 working pressure ranges, this effective etching rate must be increasing with increasing plasma power up to 100kW extractable from various gas plasma generation techniques such as dc (direct current), ac (alternating current), and ecr (electron cyclotron resonance) plasma.

10 Also the effectiveness of this process was successfully demonstrated in the etching experiments of uranium oxide on the zirconium alloys, stainless steels, or inconels (Ni based alloys) substrates.

15 BRIEF DESCRIPTION OF THE DRAWINGS

These figures are described in the Examples described in the following section.

Figure 1 is UO_2 surface morphology changes by SEM with (a) no reaction, (b) 80%CF_4-20%O_2, (c) 90%CF_4-10%O_2, and
20 (d) 60%CF_4-40%O_2 plasma reaction.

Figure 2 is UO_2 etching reaction rate vs. O_2 mole fraction at 290℃(total flow rate: 50sccm, reaction time: 100min.)

Figure 3 is UO_2 etching reaction rate vs. O_2 mole

5 fraction at 150W (total flow rate: 50sccm, reaction time: 100min.)

Figure 4 is UO_2 etching reaction rate vs. N_2/CF_4 mole fraction with the maintenance of the optimum CF_4/O_2 ratio at 290℃.

10

DETAILED DESCRIPTION OF THE INVENTION

This invention is for the effective etching or removal, i.e., decontamination of radioactive residual materials of fresh/spent nuclear fuel on the substrate

15 surface of claddings, tubes, and containers in the various systems in the nuclear facilities such as nuclear power plants, nuclear fuel factories, spent fuel dry processing laboratories, and nuclear hot cells.

Actinide elements such as thorium, uranium, and

20 plutonium are called fluorine-hungry atoms (which means

that chemical reactivity is extremely strong) and lots of fluorine atoms or molecules can be discharged in the fluorine-containing gas plasma. Based on these facts, an effective dry etching process of actinide oxides including
5 UO_2 and TRU oxide in $CF_4/O_2/N_2$ plasma has been determined in this work.

From the elementary reaction point of view, the molecular and/or atomic fluorine produced in the plasma or dissociated from the intermediate species are believed to
10 take part in the fluorination reaction. In fact, CF_4/O_2 is one of the most popular gas mixtures used for fluorination of solids in the various industries [I.C. Plumb and K.R. Ryan, *Plasma Chemistry and Plasma Processing*, **6** (1986) 205, and D.L. Flamm, V.M. Donnelly, and J.A. Mucha, *J. Appl. Phys.*, **52** (1981) 3633]. Thus, as
15 a result of its popularity, a number of studies on the gas phase reaction of the mixture gas plasma have been carried out [I.C. Plumb and K.R. Ryan, *Plasma Chemistry and Plasma Processing*, **6** (1986) 205, D.L. Flamm, V.M. Donnelly, and J.A. Mucha, *J. Appl. Phys.*, **52** (1981) 3633, J.C. Martz, D.W. Hess, J.M. Haschke, J.W. Ward, and B.F.
20 Flamm, *J. Nucl. Mater.*, **182** (1991) 277, and Y. Kim, J. Min, K. Bae, and M.

Yang, *J. Nucl. Mater.*, **270** (1999) 253].

In the current investigation, uranium dioxide was chosen as a representing actinide and its reaction rates were investigated as functions of $CF_4/O_2/N_2$ ratio, plasma
5 power, substrate temperature, and exposure time to the plasma.

Under plasma power up to 2 kW, etching reactions were examined with various CF_4/O_2 ratios for 100 minutes at several substrate temperatures of up to 600℃.

10 It is found that there exists an optimum CF_4/O_2 ratio for the effective etching in $CF_4/O_2/N_2$ plasma. The ratio of CF_4 to O_2 is around four, regardless of plasma power, substrate temperature, and gas volume flow rate.

15 Example 1.

As an example of the findings, the experimental results are plotted in Figures 1 to 3. Figures 1 and 2 reveal that the optimum CF_4/O_2 ratio for the efficient etching of UO_2 is around 4, regardless of plasma power and
20 substrate temperature. In Figure 3, UO_2 surface morphology

changes by SEM is shown as CF_4/O_2 ratio varies. The best-etched surface morphology is seen in Figure 3(b), which demonstrates that the etching rate is maximized at about $CF_4/O_2 = 4$.

5 The existence of the optimum gas composition is supported by additional surface analysis using SEM, XPS and XRD. This optimum gas composition is explained by the following experimental findings: at oxygen gas composition of lower than the optimum, the amount of oxygen is not 10 enough to pick up the carbon residuals, hence, the carbon residuals decomposed from CF_4 may deposit on the surface and suppress surface reaction, on the other hand, at higher oxygen gas composition, high reactivity of excessive oxygen with surface uranium atoms may form 15 hyper-stoichiometric uranium oxides instead of carbon mono- or di-oxide and thus interfere with the formation of volatile uranium fluorides.

XPS analysis also confirms that UO_2F_2 compound forms as a precusor intermediate on the surface during the reaction 20 and additional experiments show that reaction kinetics

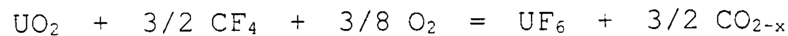
follows a linear rate law.

Example 2

When the small amount of N_2 gas, ranging from 1% to 20%
5 of CF_4 gas based on the gas volume, is added to or mixed with the optimized CF_4/O_2 gas mixture plasma the UO_2 etching reaction rate remarkably is enhanced. Experimental result in Figure 4 is an example of the enhancement of the etching rate. More specifically, under these conditions,
10 the etching rate at 290℃ is improved over 4 up to 5 times compared to that of optimum CF_4/O_2 plasma without nitrogen whose etching reaction rate is about 670 monolayers/min., (equivalent to 0.27 μm/min.). Therefore, in this case, the accelerated etching reaction rate at the same
15 temperature under same power exceeds 2500 monolayer/min., equivalent to 1.0 μm/min.

According to mass spectrometric analysis, it is determined that the major reaction product is uranium hexa-fluoride, UF_6. Therefore, based on the experimental
20 findings the dominant overall reaction of uranium dioxide

in $CF_4/O_2/N_2$ plasma is determined:



$$UO_2 + 3/2\ CF_4 + 3/8\ O_2 = UF_6 + 3/2\ CO_{2-x}$$

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

It seems that the added nitrogen plays only a catalytic
5 role in the overall surface reaction between uranium atoms and fluorine atoms or unstable fluorine-atom-containing species without changing the reaction paths or mechanisms.

This optimum etching process must be applicable to the dry etching of other actinide oxides including TRU
10 (TRans-Uranium) oxides and their mixed oxides since all actinide elements have very similar chemical characteristics with uranium and, thus, form very similar types of oxides.

In current examination, r.f. and microwave power gas
15 plasma generation techniques were used with the power ranging 50W up to 2kW and the effectiveness of this process was confirmed. Since basic principle of gas plasma generation techniques is identical except different working pressure ranges, this effective etching rate must
20 be increasing with increasing plasma power up to 100kW

extractable from various gas plasma generation techniques such as dc (direct current), ac (alternating current), and ecr (electron cyclotron resonance) plasma.

Also the effectiveness of this process was
5 successfully demonstrated in the etching experiments of uranium oxide on the zirconium alloys, stainless steels, or inconels (Ni based alloys) substrates.

By applying this effective dry-etching process, the decontamination of radioactive residual materials of
10 fresh/spent nuclear fuel on the substrate surface of claddings, tubes, or containers in the various systems can be effectively, remotely, and safely performed without introducing wet-processing in the nuclear facilities in which contaminations can take place by the residuals of
15 fresh or spent nuclear fuel.

CLAIMS

1. A process for gas-phase etching of actinide oxides from a substrate by using plasma power comprising the
5 steps of;

a) preheating actinide oxides on the substrate within a process chamber filled with fluorine-containing gas and exposing it to plasma power, and subsequently

b) etching actinide oxides from the substrate using a
10 plasma gas-phase reactant system.

2. The process of claim 1 wherein the actinide oxides are ThO_2, PaO_2, UO_2, NpO_2, PuO_2, AmO_2, CmO_2, BkO_2, CfO_2, and their mixed oxides.

15

3. The process of claim 1 wherein the substrate is made of zirconium alloys, stainless steels, or inconels (Ni based alloys).

20 4. The process of claim 1 wherein, in step a), the

fluorine-containing gas is in a mixture of carbon tetra-fluoride, oxygen, and nitrogen and the volume ratio of oxygen to carbon tetra-fluoride is from about 15:85 to about 25:75.

5

5. The process of claim 4 wherein the fluorine-containing gas is in a mixture with 1% up to 20% N_2 of CF_4 gas based on the gas volume in the process chamber.

10

6. The process of claim 1 wherein, in step a), the plasma power sources are r.f. (radio frequency), dc (direct current), ac (alternating current), micro-wave, and ecr (electron cyclotron resonance) plasma power.

15

7. The process of claim 1 wherein, in step a), the plasma power is from about 50W to 100kW.

8. The process of claim 1 wherein, in step b), the

20 gas-phase reactant system further comprises a catalyst.

9. The process of claim 1 wherein, in step b), the substrate temperature is from about ambient temperature up to about 600℃.

5

10. The process of claim 1 wherein, in step b), the pressure in the process chamber during plasma gas-phase etching step is from about 1 mTorr up to about 1 atm pressure.

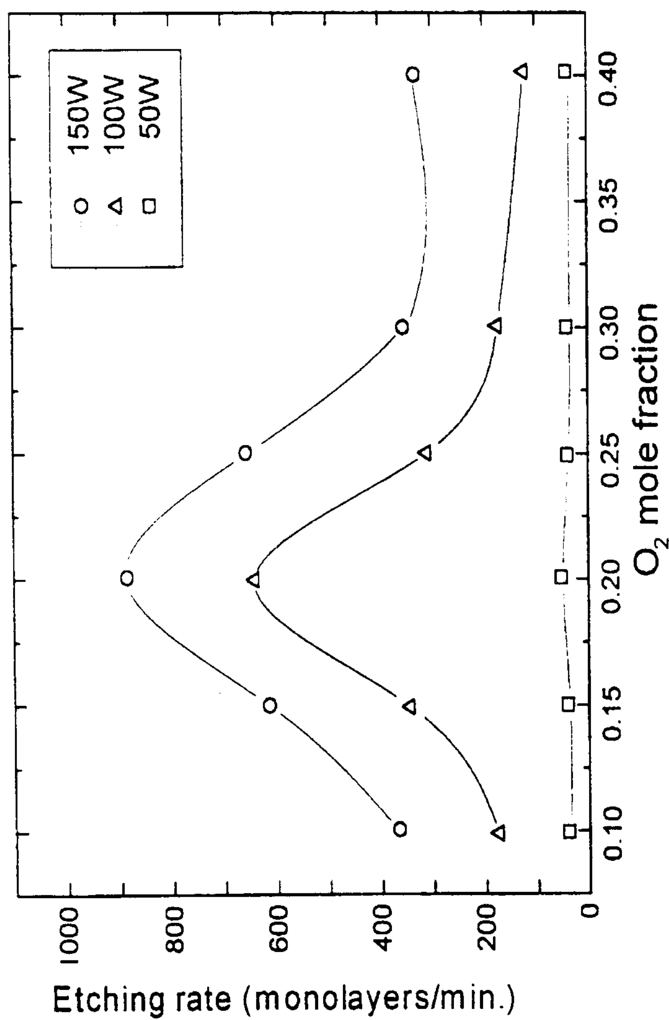
10

11. The process of claim 10 wherein, in step a), constituent gases in the fluorine-containing gas are provided separately to the process chamber in the separate carbon tetra-fluoride, oxygen, and nitrogen gas supply

15 lines controlled by respective mass flow controllers with flow rates ranging from 10 sccm to 1000 sccm or optionally supplied to the process chamber in admixture of carbon tetra-fluoride, oxygen and nitrogen in a flowing gas regime with the total gas flow rate from 10 sccm to about

20 1000 sccm.

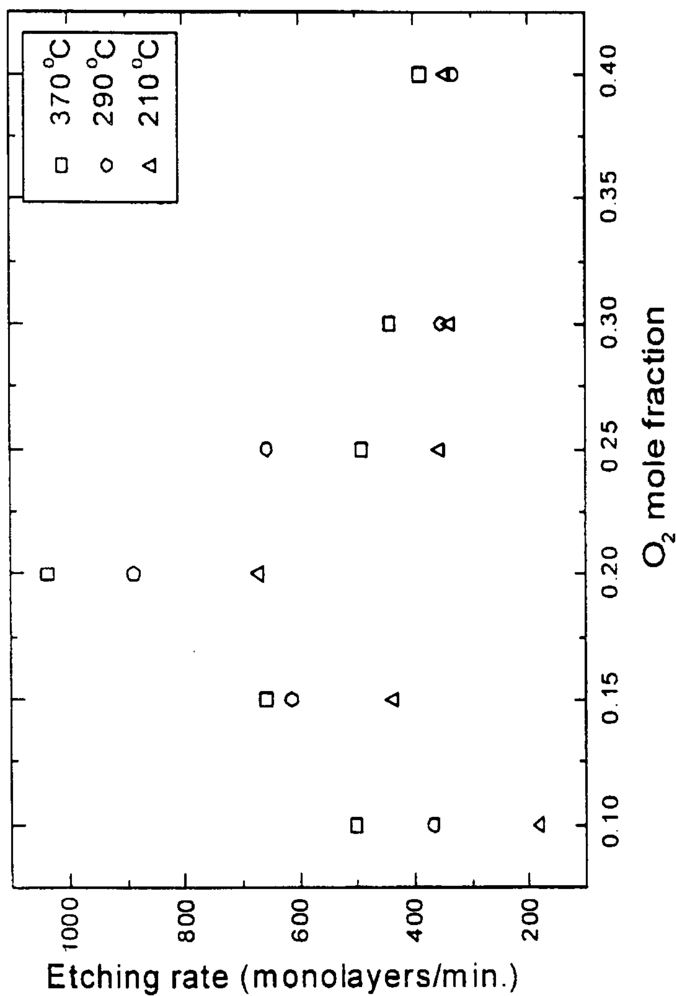
FIG. 1



UO_2 etching reaction rate vs. O_2 mole fraction at 290 °C

(total flow rate: 50sccm, reaction time: 100min)

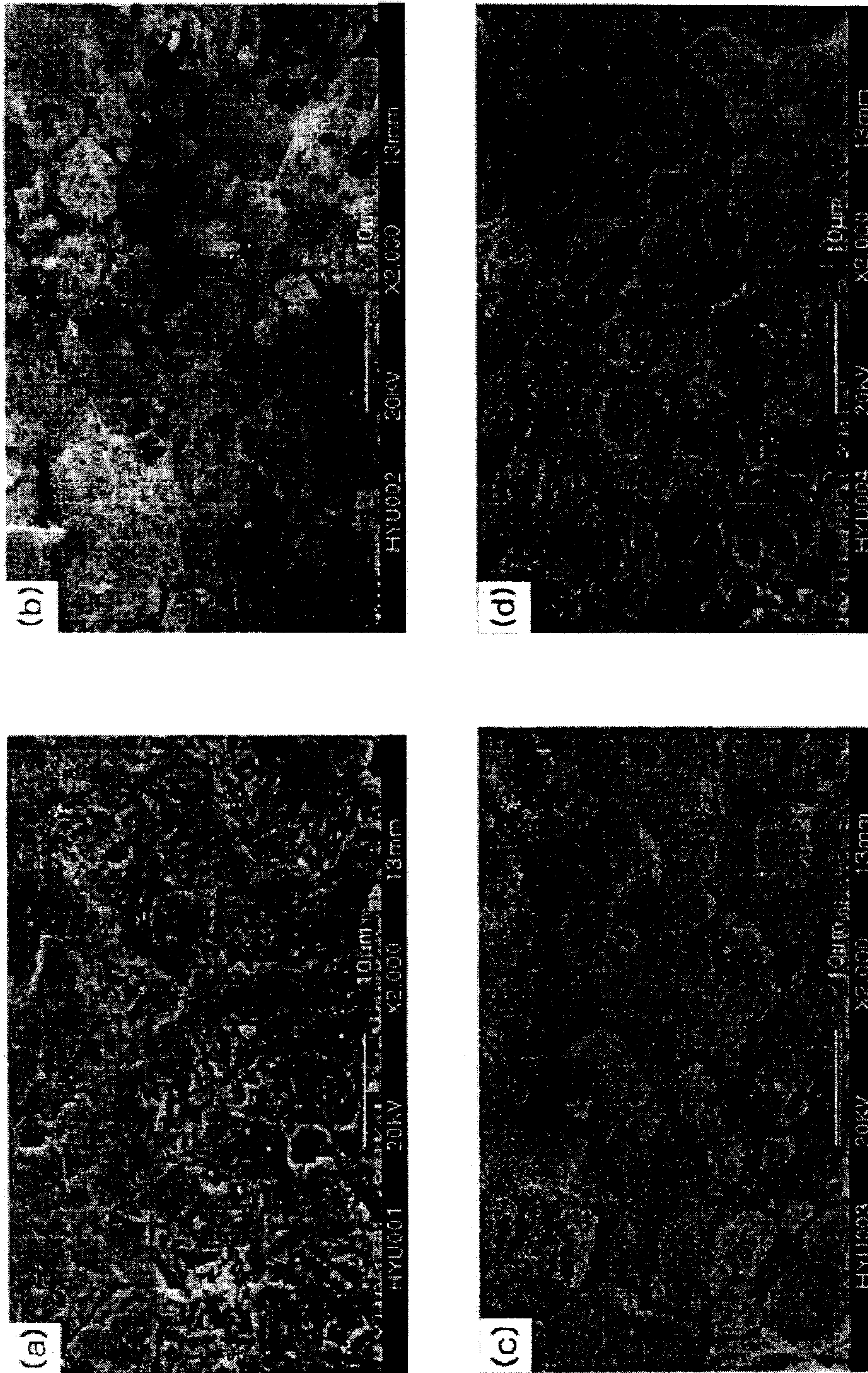
FIG. 2



UO_2 etching reaction rate vs. O_2 mole fraction at 150W

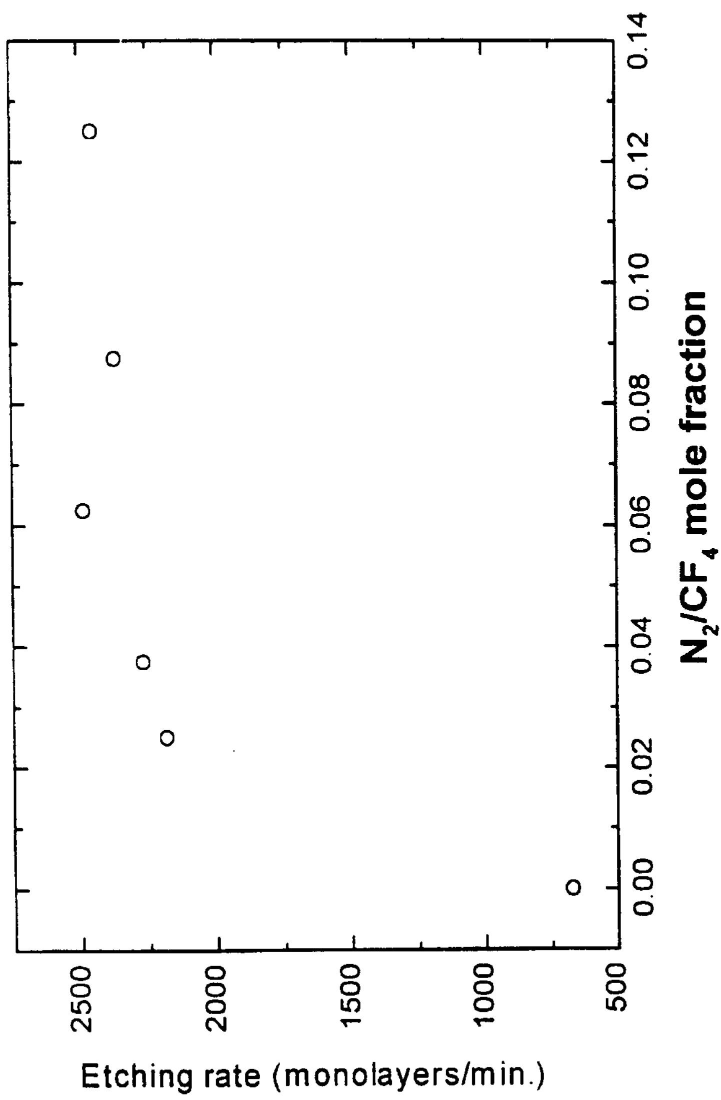
(total flow rate: 50sccm, reaction time: 100min)

FIG. 3



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

FIG. 4



UO_2 etching reaction rate vs. N_2/CF_4 mole fraction with the maintenance of the optimum CF_4/O_2 ratio at 290℃

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC[7]: G 21 F 9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7]: G 21 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel-WPI, STN-CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4797178 A (BUI et al.) 10 January 1989 (10.01.89), totality.	1-11
A	TATENUMA K. "Newly developed decontamination technology based on gaseous reactions converting to carbonyl and fluoric compounds". Nucl. Technol., 1998, 124(2), pages 147-164, (abstract), Retrieved from: STN International, Columbus, Ohio, USA, STN-CA Accession No. 130:30453.	1-11

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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„O" document referring to an oral disclosure, use, exhibition or other means
„P" document published prior to the international filing date but later than the priority date claimed
„T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
„X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00301

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US A 4797178	10-01-1989	EP A2 298204	11-01-1989
		EP A3 298204	20-12-1989
		JP A2 63317683	26-12-1988