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Author(s): John M. Veilleux
Carter Munson
John Fitzpatrick
E.P. Chamberlin
M.S. El-Genk

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PLASMA DECONTAMINATION OF URANIUM FROM THE INTERIOR OF ALUMINUM OBJECTS

John M. Veilleux[1] and Mohamed S. El-Genk
Institute for Space and Nuclear Power Studies
Chemical and Nuclear Engineering Department
University of New Mexico
Albuquerque, NM 87131

Carter Munson, Physics Division
E. P. Chamberlin and J. Fitzpatrick
Chemical, Science & Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87544

Abstract

RF plasma glow discharges are being investigated for removing and recovering radioactive elements from contaminated objects, especially those contaminated with transuranic (TRU) materials. These plasmas, using nitrogen trifluoride as the working gas, have been successful at removing uranium and plutonium contaminants from test coupons of stainless steel and aluminum surfaces, including small cracks and crevices, and the interior surfaces of relatively hard to reach aluminum pipes. Contaminant removal exceeded 99.9% from simple surfaces and contaminant recovery using cryogenic traps has exceeded 50%. Work continues with the objective of demonstrating that transuranic contaminated waste can be transformed to low level waste (LLW) and to better understand the physics of the interactions between plasma and surface contaminants. This work summarizes the preliminary results from plasma decontamination from the interior of aluminum objects—the nooks and crannies experiments.

INTRODUCTION

The Department of Energy (DOE) has a large, and growing, array of tools and components contaminated with plutonium—the bulk of transuranic (TRU) waste—and uranium that have accumulated during the development and assembly of the nation's nuclear stockpile. Current decontamination techniques involve significant personnel contact with waste material, and generation of significant quantities of secondary liquid waste, which must be treated in some fashion. The DOE complex had 256,000 cubic meters of TRU waste in 1991 which is expected to grow to 845,000 cubic meters by 2000 (Kisieleski et al.). Cost of treatment, storage, and disposal varies by type of waste. Typical costs of treatment (acid rinses, mechanical scrubbing with detergents, etc.) have been estimated (Allen and Hazelton, 1984) at $4,500 per cubic meter after allowing for inflation. Storage costs range from $3,700 per cubic meter for contact handled TRU waste to $37,400 per cubic meter for remote handled TRU waste. Disposal costs range from $22,000 to $28,000 per cubic meter for transuranic (TRU) waste compared to $1,200 to $1,800 per cubic meter for low level waste (LLW).

Plasma based processes for removing plutonium and uranium surface contaminants from metallic components (glove boxes, tools, pipes, etc.) would provide a significant advantage. Plasma systems can be operated remotely and therefore do not require direct human contact with the waste. Using a cryogenic distillation technique, the radioactive metal hexafluoride gas is recovered in a liquid nitrogen trap from whence it may be converted to either the liquid or solid form. Even if plasma decontamination can be used for only 10% of the TRU waste (e.g., high value items, tools, etc.), a net savings of over one billion dollars could be realized by eliminating only the disposal costs. The development of plasma systems can thus be justified on the basis of reduction of personnel exposure, minimization of secondary waste streams, and cost savings.

Martz et al. (1991) conducted the initial work of plutonium etching in a low power (50W) CF_4/O_2 RF plasma operated at low pressures (13 to 65 Pa). He reported etch rates of 1 to 6 Angstrom per second for Pu and PuO_2, respectively, which equates to 0.007 kg/(hr-m^2) for Pu metal and 0.025 kg/(hr-m^2) for PuO_2. The present work is an outgrowth of these plutonium experiments. Experiments using milligram amounts of depleted uranium (~0.002% ^{235}U) as well as nanogram amounts of fissile uranium (^{233}U) have been conducted on stainless steel and aluminum substrates. Subsequent work on the interior of aluminum objects—the nooks and crannies hidden from sputtering and reactive ion etching—was also performed. This paper presents the preliminary results of these latter experiments.

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[1] Corresponding Author, MS J514, Los Alamos National Laboratory, Los Alamos, NM 87544

THEORY

Etching of plutonium and uranium actinides by fluorine bearing gases takes place via several steps (Fig. 1). First, RF power is transferred to the gas thereby causing ionization and the initiation of a glow discharge plasma. The highly mobile electrons collide with the heavier neutrals and other ions thereby causing ionization and excitation. Collisions with the NF_3 molecules result in the dissociation of these molecules into several species, including atomic fluorine, F, and ionic species, such as F^+ and NF_2^+. The atomic fluorine atoms are highly reactive and diffuse to surfaces where they undergo chemical reactions with uranium, such as the cascade reactions[*] :
UF, UF_2, UF_3, UF_4, UF_5, and

Figure 1. Plasma Etching Of Uranium Dioxide.

Properties
U - 3.55A diameter
F - 0.8A diameter
Unit Cell--5.5A

Desorption

Adsorption

Substrate

UF_6. In the reactive ion etching mode, positive ionic species, such as the F^+ and NF_2^+, are accelerated through the plasma sheath where they collide with surface sites (e.g., UO_2 molecules) to break chemical bonds and to further react with uranium and thus increase reaction rates by factors of 10 or more (Lieberman, 1994) above the diffusion only rates. In crevices and other areas hidden from the plasma, the reactions rely mostly on diffusing atoms to react with the surface contaminants. Thus, reactive ion etching is not a major contributor to the reaction rate in these instances. Figure 1 shows the etching of uranium dioxide (UO_2) in its face-centered cubic crystal lattice into uranium hexafluoride (UF_6). Once the uranium atom is fully fluorinated with six F atoms, the volatile UF_6 molecule can be pumped away. In addition to uranium, this process also applies to plutonium and its compounds which are also volatile and react with fluorine to form gaseous plutonium hexafluoride.

Figure 2. Plasma Chamber and Recovery System.

Plasma System

Recovery System

13.56Mhz Supply & Matching Network

NF3

Sample

Cathode

High Speed Pumps

1 - Cold Trap Finger
2 - Charcoal Trap
3 - Cold Trap Isolation Valves

Forepump

EXPERIMENTAL SETUP

The plasma etch and recovery system is shown in Fig. 2. The volume of the plasma chamber is 125 L. The source of fluorine is NF_3 gas flowing at 0.2 to 0.4 L/min to maintain a glow discharge at pressures in the range of 7 to 20 Pa. A 13.56 MHz RF power source (RF Plasma Products RF20, 2000W, 15A) provides the energy to create and maintain the plasma. Typical operating power has been in the vicinity of 100W. The uranium source is located on the powered cathode in these experiments. The plasma chamber is initially pumped down with a high speed forepump and roots blower (Leybold D30 and WS-150, respectively) then the

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[*] The stable compounds are with three or more atoms of fluorine (Katz et al.: p301).

pumping is subsequently transferred to the recovery system forepump. The NF_3 gas is introduced at flow rates of 0.2 - 0.4 L/min and the plasma initiated. A matching network (Heathkit Antenna Tuner SA2060) is used to maximize power transfer to the plasma. The plasma potential with respect to ground is monitored during etch operations. During the etching process, vacuum is maintained via the recovery system forepump (Alcatel 2008A, item 4) so that any radioactive gases are trapped. The recovery system is completely installed in a fume hood for this experimental application. A liquid nitrogen cooled trap (item 1) is used to recover the metal hexafluoride. A small amount of water and/or nitric acid is introduced into the cold trap prior to etch operations so that the radioactive gas will react to form a liquid or solid when the cold trap is warmed to room temperature. For example, trapped UF_6 will react to form a liquid uranyl nitrate solution. When etch operations are complete, two valves (item 3) are closed to isolate the cold trap for removal and recovery of the contents. A charcoal trap (item 2) is also installed between the Alcatel 2008A forepump (item 4) and the cold trap to prevent forepump oil from back diffusing and to trap fluorine to prevent it from seizing the pump bearings.

Uranium Samples

Samples used to measure the etch process are from solutions of depleted uranium in the form of uranyl nitrate, $UO_2(NO_3)_2 \bullet xH_2O$, where x ranges from 2 to 6. The solution contains over 99.9% ^{238}U with negligible amounts of ^{234}U and ^{235}U. The molarity of the solution was determined by liquid scintillation counting in a Packard Instrument Company Model 2200CA. Comparison with other methods (gravimetrically and alpha scintillation counting) were in agreement.

The mass of the ^{238}U in the uranyl nitrate solution forms the basis to assess plasma decontamination capability. Preparation of a sample involves pipetting a volume of solution onto a substrate and the solution dried, leaving a mixture of solid uranyl nitrate and oxides of uranium. Comparison of the mass of ^{238}U in the sample before and after plasma etching is used as the basis for determining etch rates. Because the initial sample deposits are too thick to prevent substantial alpha particle self-shielding, the initial ^{238}U mass determination was obtained from the volume of solution pipetted and the previously calculated molarity of the solution. Weighing was not used because it leads to high relative mass errors at the milligram quantities used due to the uncertain composition of the oxides and time dependent mass changes due to the rapid hydrolysis of the uranyl nitrate. Final mass estimates were obtained from alpha particle counting since self-shielding following plasma etching was generally found to be minimal.

Molarity Determination

The molarity of the solution was determined by three methods: liquid scintillation counting (LSC), weighing, and by alpha particle scintillation counting. Liquid scintillation of solution volumes ranging from 10 to 100 microliters led to the best determination of solution molarity, 0.55 ± 0.08 mol/L (one sigma). Weight measurements taken after drying the solution led to results similar to those determined by LSC (0.5 ± 0.25 mol/L) but with higher standard deviations. Weight measurements are prone to considerable error because the exact form of the uranyl compound is believed to be a mixture of crystallized uranyl nitrate dihydrate, uranyl nitrate hexahydrate, and uranium dioxide with the latter probably being the predominant compound. Weight errors are minimized when the measurements are taken just after heating on a high setting. Alpha particle counting was evaluated over a range of pipetted uranyl nitrate solutions and found to lead to the smallest self-shielding when pipetted volumes were less than two microliter per cm^2. Actual initial sample sizes used in these experiments were in the vicinity of 30 to 100 microliter/cm^2, well above this maximum. Consequently, calculation of mass from alpha activity is much lower for initial mass estimates. Assuming that UO_2 is the predominant material remaining following etch operations, the calculated surface thickness from activity measurements are smaller that the penetration range of the 4.2 MeV ^{238}U alpha particle (Friedlander), thus minimizing self-shielding effects. In calculating mass of ^{238}U from activity, corrections are also made for the efficiency (42%) of the calibrated alpha scintillation counter and the activity ratio of ^{238}U to other isotopes (0.874) in the solution. The masses of the other isotopes are neglected since they are in the nanogram range compared to the milligram range for ^{238}U.

Substrate Materials

Substrate materials used for these experiments are type 6061-T6 aluminum holders depicted in Fig. 3. Two holders are placed face-to-face to provide a crevice whose dimensions are 1 by 2 cm with an opening of 0.09 cm.

Test parameters and methods

The uranyl nitrate solution is deposited in the crevice of one side of the aluminum holder with an Eppendorf Series 2000 adjustable volume pipette, evaporated on medium heat using a heating plate, and then heated on high setting for at least 5 minutes until the precipitate turns burnt orange. Next, the total activity is measured. An integral spectrum of activity is then obtained by covering a portion of the crevice with an aluminum measuring device. Counts are made with the device exposing more and more crevice area. The counting procedure is followed both before and after plasma processing.
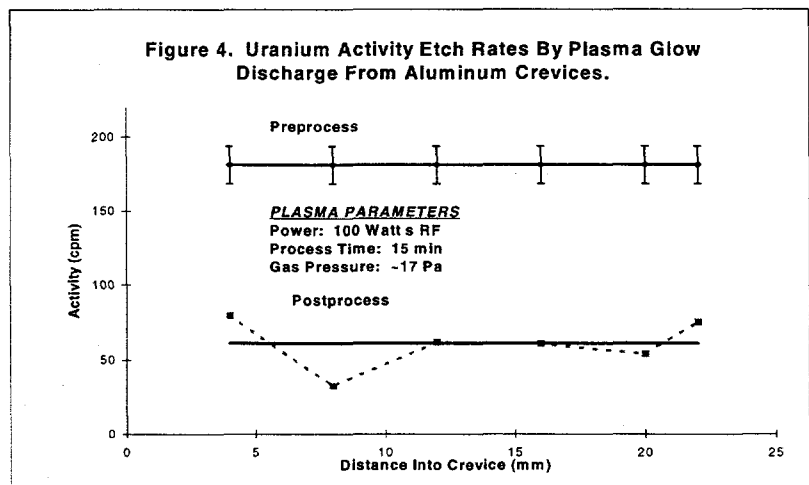
Figure 3. Sample Holders For Plasma Experiments.

6.4 cm

5 cm

1 cm

2 cm

Thickness ~ 0.16 cm

Crevice ~ 0.045 cm

Aluminum Sample Holder
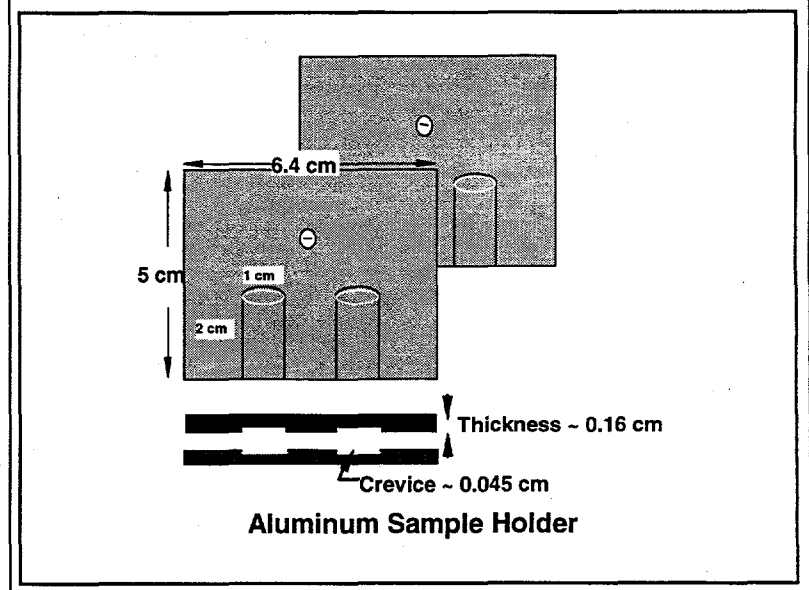
RESULTS AND DISCUSSION

Typical activity removal rates as a function of distance into the aluminum crevice are depicted in Fig. 4. The measured activity in counts per minute (corrected for background, but not instrument efficiency nor self-shielding) indicates that the preprocessing activity (prior to plasma treatment) is relatively constant and uniform at 180 cpm along the crevice (top, solid line). The one sigma relative error bars are shown for both sets of activities. After processing the sample in plasma for 15 minutes at 100 W, the activity is reduced to an average of 60 cpm (solid line), or 66% activity removal, with somewhat more activity remaining at the mouth of the crevice (dashed line). The mass etch rates, with alpha particle self-shielding accounted for, leads to initial mass removal rates of approximately 0.2 kg/hr-m^2 and mass removal percentages of 88%.

Figure 4. Uranium Activity Etch Rates By Plasma Glow Discharge From Aluminum Crevices.

Preprocess

PLASMA PARAMETERS
Power: 100 Watt s RF
Process Time: 15 min
Gas Pressure: ~17 Pa

Postprocess

Activity (cpm)

Distance Into Crevice (mm)

As activity is removed from the crevice, there appears to be an exponential reduction in the mass etch rate (Fig. 5). Mass removal rate drops from 0.2 kg/hr·m^2 at 15 minutes processing time to 0.1 kg/hr·m^2 at 30 min, 0.05 kg/hr·m^2 at 60 minutes, and 0.02 kg/hr·m^2 at 120 min. This may be representative of fewer surface sites for the active fluorine species to react with as the surface activity is removed, or to some other rate limiting process. Visually, after two hours of processing, most of the uranyl nitrate is gone. The exponential character of the curve, with an initial high rate coefficient with a time constant of 34.2 minutes increasing to 54.1 minutes (solid curve) for the overall rate, suggests a transition event. A surface film of UF$_6$ may form opposing the ability of fluorine atoms to diffuse to the surface site. Or perhaps thick localized deposits, or "islands", of uranium compounds occur in preparing the sample such that the reaction surface is initially large and decreases with time as only the "islands" remain. In any event,

some rate limiting diffusion event occurs to cause the change in etch rate with process time. Further experimentation is needed to resolve this question.

On simple (flat) stainless steel planchettes, removal rates exceeded 99.9% based strictly on activity measurements without correction for alpha particle self-shielding. These experimental results must be revisited to make comparisons with the crevice data. We believe that uranium removal rates will probably be much greater (factors of 10 or more) on flat surfaces because both reactive ion etching and fluorine chemistry play roles instead of chemistry alone as in the crevices.

Figure 5. Uranium Mass Etch Rates By Plasma Glow Discharge In Aluminum Crevices

INITIAL RATE
$dm/Adt = 0.24e^{-t/34.2}$
Time Constant = 34.2 min

PLASMA PARAMETERS
Power: 100 Watt RF

OVERALL RATES
$dm/Adt = 0.15e^{-t/54.1}$
Time Constant: 54.1 min

SUMMARY & CONCLUSIONS

The successful removal of uranium contamination from crevices in aluminum substrates by fluorine plasma glow discharges has been demonstrated. Mass removal rates of 0.2 kg/hr/m² have been observed with exponential decreases in rates with increasing process times as rate limiting effects take place. Determination of these rates must take into account self-shielding of alpha particles to obtain an accurate removal rate. The etch rate is primarily dependent on the chemistry of fluorine with uranium since other processes, namely, reactive ion etching and sputtering contributions from acceleration of ions through the plasma sheath, are small.

ACKNOWLEDGEMENT

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