Proceeding of the Korean Radioactive Waste Society
Vol. 2(1), June 2004

Removal of Metallic Cobalt Layers by Reactive Cold Plasma

Yong-SooKim, Sang-HwanJeon, Byung-JooYim, andHyo-CheolLee
Jong-HeonJung* and Kye-NamKim*
Hanyang University, 17 Haengdang-Dong, Sungdong-Gu, Seoul
* Korea Atomic Energy Research Institute, 150 Duckjin-Dong, Yusung-Gu, Daejeon

Abstract

Recently, plasma surface-cleaning or surface-etching techniques have been focused in respect of the decontamination of spent or used nuclear parts and equipment. In this study the removal rate of metallic cobalt surface is experimentally investigated via its surface etching rate with a CF_4-O_2 mixed gas plasma. Experimental results reveal that a mixed etchant gas with about 80% CF_4-20% O_2 (molar) gives the highest reaction rate and the rate reaches 0.06 μm/min at 380 °C and ion-assisted etching dramatically enhances the surface reaction rate. With a negative 300 V DC bias voltage applied to the substrate, the surface reaction initiation temperature lowers and the rate increases about 20 times at 350 °C and up to 0.43 μm/min at 380 °C, respectively. Surface morphology analysis confirms the etching rate measurements. Auger spectrum analysis clearly shows the adsorption of fluorine atoms on the reacted surface. From the current experimental findings and the results discussed in previous studies, mechanistic understanding of the surface reaction, fluorination and/or fluoro-carbonylation reaction, is provided.

Key Words : Decontamination, Cobalt-Layer, Plasma Surface Cleaning, Ion-Assisted Etching

I. Introduction

Under continuous power operation, many major parts and equipment in nuclear power plants are gradually surface contaminated by the absorption or adsorption of radioactive isotopes. If these surface contaminants can be removed selectively, it should be possible to convert the radioactive substrate metal into a non-radioactive or low-level radioactive material. This would lead to a tremendous volume reduction of radioactive wastes and to substantial economic gain from the recycled substrate materials. Recently OECD/NEA claimed that approximately 30 million tons of contaminated metal scraps would be produced over the next 50 years from dismantling and decommissioning nuclear facilities.[1] IAEA also reported that dismantling of one Russian RBMK 1000 reactor would generate nearly 35,000 tons of Cr-Ni steel.[2]

Metal surface cleaning using reactive plasma gas is one of the emerging dry processing techniques applicable to high-bonding-energy contaminants. This technique can fulfill the

requirement of minimum secondary waste generation while maintaining the same levels of efficiency as conventional wet decontamination techniques.[2,3] In principle, the technique selectively turns the surface contaminants into volatile compounds through catalytic surface reactions and evaporates them out of the surface. Basically the radioactive contaminants can be categorized into three groups: uranium compounds and trans-uranic (TRU) elements released from the nuclear fuel rods corrosion products such as Co, Fe, Ni and Cr produced during the aqueous corrosion of metallic parts and fission products such as Mo, Tc, Ru, and Rh generated in fission reactions.

Since the early 1990s, several studies of this new technique have been reported in nuclear applications using various plasma sources.[4-12] Recently, plasma surface-cleaning or surface-etching techniques have been considered for the decontamination of spent or used nuclear parts and equipment.[7-13] Fundamentally, they are the techniques for converting the surface contaminants into volatile fluorides and/or carbonyl compounds that have high volatility, or very low melting and boiling temperatures.

Among the radioactive elements, Co is one of the principal contaminants of the used metallic parts or equipment such as valves and pipes made of stainless steels or inconel alloys. The γ-ray spectroscopic result of the discharged inconel alloy tube in Figure 1 demonstrates that two isotopes, Co-58 and Co-60, are the predominant ones. Of these, Co-60 bears a special importance because of its relatively long half-life (5.27 years) and high-energy photons (1.17 and 1.33 MeV).[14] Therefore, the removal of Co isotopes from the contaminated metal surface is one of the major tasks in the development of metallic surface decontamination technology.

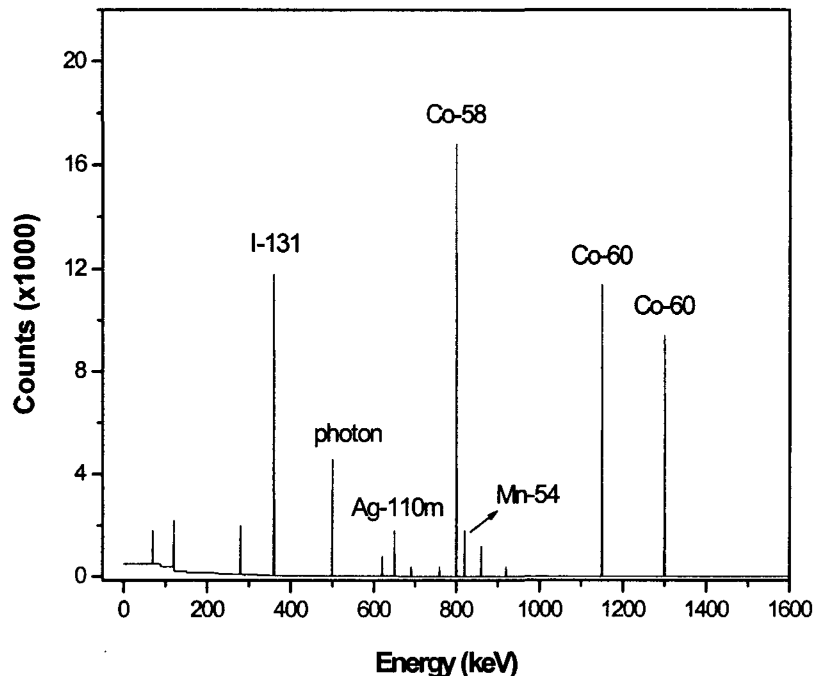


Figure 1. γ-spectroscopy results of discharged nuclear steam generator inconel alloy tube.

Lately, various plasma sources have been developed for this purpose and some successful results have been reported.[7-11] Despite these excellent demonstrations, however, the papers gave little consideration to the mechanistic understanding of the surface reaction and the decontamination process and even the optimum operation parameters or conditions were not fully determined.

In this study, therefore, metallic cobalt is chosen again as a target element and the decontamination rate of the cobalt metal is experimentally investigated via the surface-etching rate with the focus on the mechanistic understanding of the reaction and the determination of the optimum parameters. As the etchant gas, a CF_4-O_2 gas mixture is selected because it has been reported that both carbon monoxide (CO) and fluorine radicals (F) are abundantly generated in the plasma, depending on the volume ratio.10,15) In fact, they are considered reactant radicals that form volatile carbonyl and fluoride or fluoro-carbonyl compounds, which are believed to be essential gaseous products in the decontamination process.

In addition, the effects of both negative bias voltage application and elevated substrate temperature on the etching reaction are examined, as metallic Co is an irresponsive metal at less than 300 °C.[16] The bias voltage induces ion-assisted etching, which is known to be very effective, especially when the surface reaction requires high activation energy.[17-19]

To support the experimental findings, surface analysis techniques such as Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) are used as well as plasma diagnostic analysis using Optical Emission Spectroscopy (OES).

II. Experimental

First, to meet the objectives of the current study, cold plasma apparatus for metallic surface etching is designed and manufactured. Then, the experimental investigation is performed with three experimental variables: the volume ratio of CF_4 to O_2 in the binary etchant gas mixture, the specimen substrate temperature, and the bias voltage applied to the specimen substrate.

As seen in Figure 2, plasma reactor is a diode type and rf power of up to 600 W can be applied between the parallel electrodes. Their distance can be adjusted, however during all our experiments, it is kept at 5 cm. Samples can be heated up to 800 °C by a halogen lamp heater in the reaction chamber. Bias voltages as great as 500 V can be applied to the substrate. The binary etchant gases, CF_4 and O_2, are supplied to the reaction chamber through mass flow controllers with fine control of their flow rates. Total gas pressure is maintained 0.45 Torr in these experiments. To avoid complicated radiation protection procedures, non-radioactive cobalt metal samples with 99.8% purity are prepared.

The prepared metal pieces are cut into thin disk specimens using a low-speed diamond wheel cutter. Prior to loading the sample to the reaction chamber, the surface of the specimen is polished to a mirror-like finish with grit 600 sandpaper, pickled in a pickling solution, cleaned ultrasonically, and baked at 200 °C for 10 minutes in a vacuum to evaporate moisture adsorbed on the surface.

The decontamination rate is estimated as the surface-etching rate, which is measured by weight loss during the reaction. These measurements are made with an electro-micro balance (BP210D, Sartorius) with a sensitivity limit of 10^{-5} g. The weight loss is expressed in units of micrometers per minute.

Along with the decontamination rate measurements, OES and AES analyses are carried out to diagnose the plasma parameters and to obtain information on the reaction mechanism.

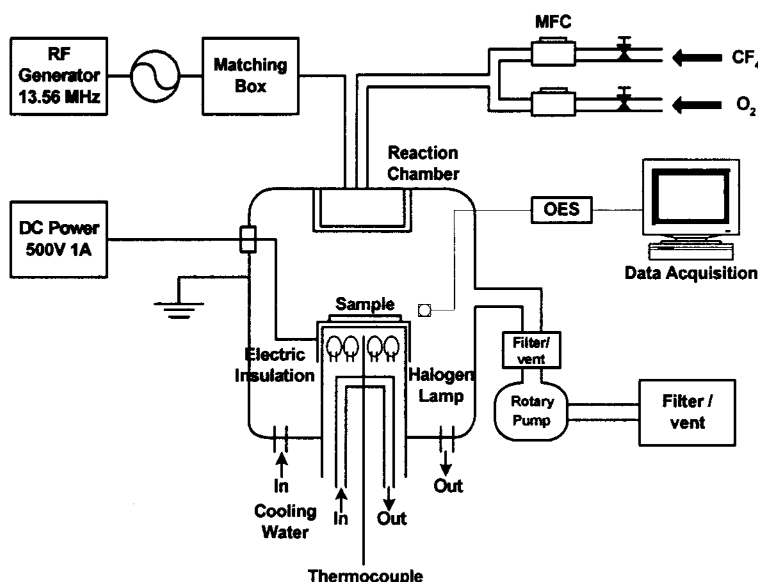


Figure 2. Schematic of cold plasma reactive ion etching apparatus.

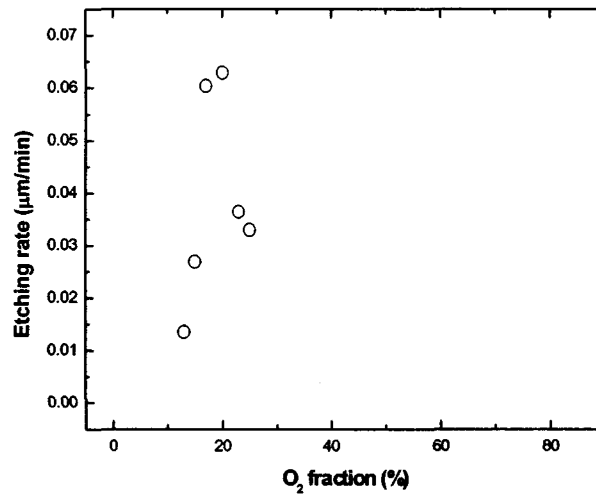
III. Results and Discussion

First, etching reaction rates are examined with various CF_4/O_2 ratios at three substrate temperatures, 290 °C, 350 °C, and 380 °C, to find the highest etching rate as a function of CF_4/O_2 ratio. In these measurements, rf plasma power and exposure duration are set to be 220 W and 120 minutes, respectively.

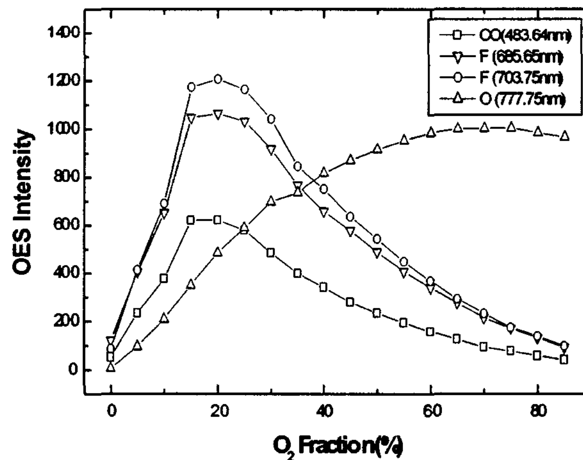
Figure 3(a) shows the results with various mole fractions of O_2 at 380 °C, revealing that about 80% CF_4 20% O_2 mixed binary gas gives the highest reaction rate and the rate reaches 0.06 μm/min. The same optimum composition is observed at other substrate temperatures, even though the effect of compositional changes becomes less distinctive at lower temperatures. This finding is supported by previous OES plasma diagnostics results with CF_4/O_2 mixture gas,[7,10] as seen in Figure 3(b). This figure demonstrates the significant role of fluorine and carbon monoxide radicals in the reaction.

In the following low-temperature measurements, it is found that there is almost no surface etching at 290 °C. However, etching begins to occur at around 350 °C and its rate increases as the substrate temperature increases above that temperature. These results are shown in Figure 4. Unfortunately, the maximum etching rate attained at 380 °C, 0.06 μm/min, is not high enough to be useful for practical decontamination. To enhance the reaction rate

with the ion-assisted etching technique, therefore, negative bias voltage is applied to the metallic cobalt substrate. Figure 4 clearly shows that the bias voltage lowers the surface reaction initiation temperature and dramatically increases the reaction rate at each substrate temperature. With 300 V DC, the reaction is measurable even at 290 °C and progresses vigorously at 350 °C. In fact, the rate increases 20 times at 350 °C and the highest etching rate achieved at 380 °C is 0.43 μm/min. Conversely this result proves that the ion bombardments induced by the negative bias voltage applied to the substrate assist the surface reaction of the metallic cobalt.



(a)

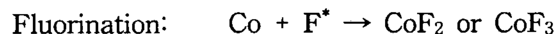


(b)

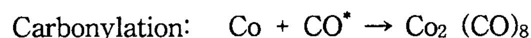
Figure 3. (a) Co etching reaction rate vs. O_2 mole fraction at 380 °C. (total flow rate: 100 sccm, plasma exposure time: 120 min, rf power: 220 W, no bias voltage, total pressure: 0.35 Torr) (b) Emission intensities of F, O and CO with O_2 mole fraction.[7]

To confirm these results, surface morphology changes before and after the reaction are examined using SEM and AFM. Figure 5 shows SEM micrographs taken before and after the reaction with and without substrate bias voltage at 350 °C, and Figure 6 presents three-dimensional AFM images of the SEM micrographs in the previous figure. The morphology changes at 350 °C evidently demonstrate that the mirror-like flat surface before the reaction becomes rough after exposure to the reactive plasma gas and the negative bias voltage turns the moderate reaction into a vigorous one. The three dimensional AFM images vividly show the progressive roughness changes.

As mentioned in the introduction, diagnosis of CF_4/O_2 mixed gas plasma by OES analysis reveals that the intensities of F and CO radicals reach a maximum at around 20% mole fraction of O_2.[10,15] In addition to these findings, the strong chemical affinities of F and CO radicals, the high volatility of fluoride compounds, and the very low melting temperature of carbonyl compounds (for example, 51 °C for $Co_2(CO)_8$[16,20]) provide support that the dominant surface reactions are fluorination and/or carbonylation. The probable basic reactions are as follows:



Fluorination: $Co + F^* \rightarrow CoF_2$ or CoF_3



Carbonylation: $Co + CO^* \rightarrow Co_2(CO)_8$

Hence, to examine the surface atoms participating in the reaction, AES analyses are carried out before and after the reaction. One of the results is shown in Figure 7. The first figure (a) shows the AES spectrum of the intact Co specimen, which is in good agreement with the standard cobalt spectrum[21] except for carbon and oxygen peaks. The carbon peak is from the residuals on the surface that always reside in the vacuum system. The two oxygen peaks must be from an oxide layer on the specimen surface. Even though relatively thick oxide was

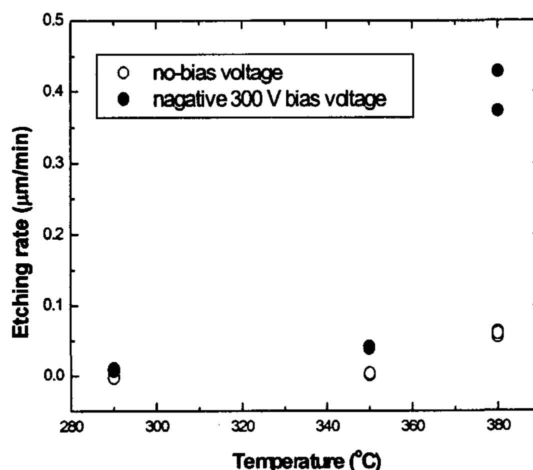


Figure 4. Co etching rate vs. various substrate temperatures (total flow rate: 100 sccm, reaction time: 120 min., 20% O_2 mole fraction, rf power: 220 W, bias: -300 V, total pressure: 0.35 Torr)

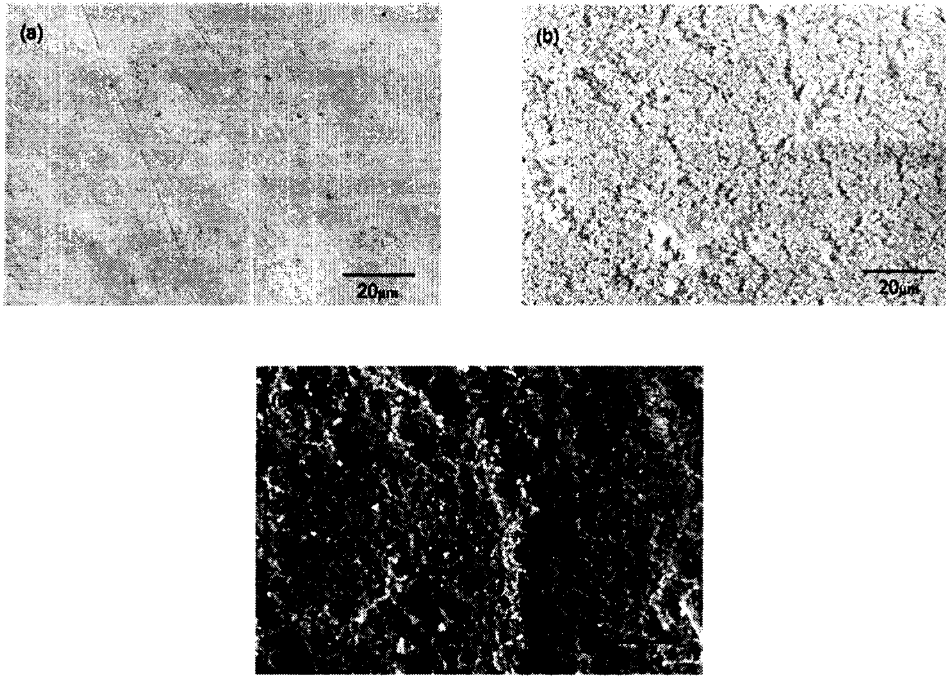


Figure 5. SEM micrographs of surface morphology changes before and after surface reaction at 350 °C (a) intact (b) no-bias voltage (c) -300 DC bias voltage

removed with the pickling solution prior to the specimen loading in the reaction chamber, it turns out that a few monolayers of thin oxide film inevitably form on the metal surface because of the high oxygen potential in the ambient environments. However, the post-reaction AES spectrum plotted in Figure 7(b) shows only Co atom peaks without the carbon and oxygen peaks. This supplementally proves that the current surface etching reaction can eliminate even an oxide layer on the surface.

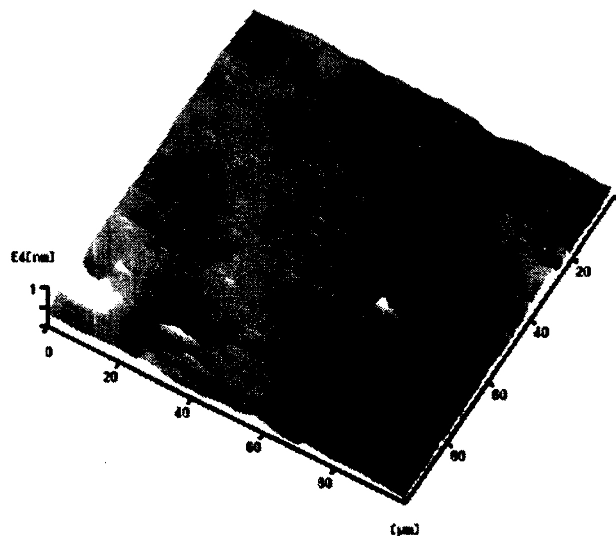
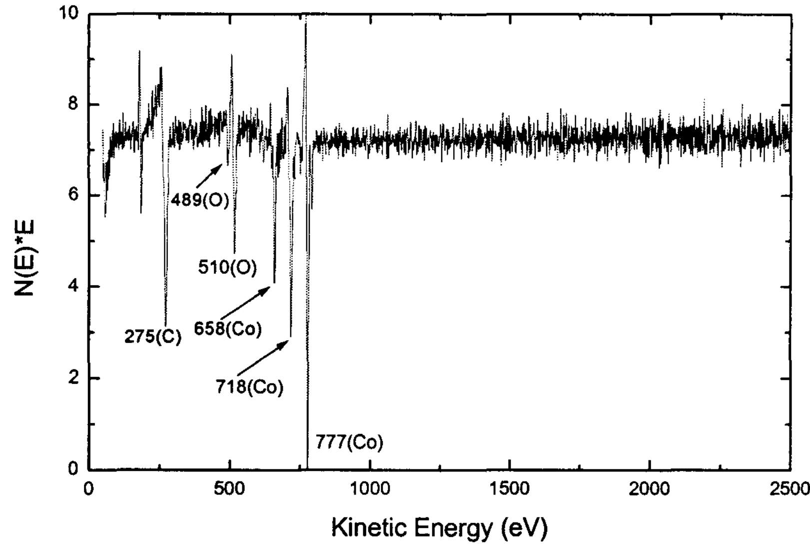
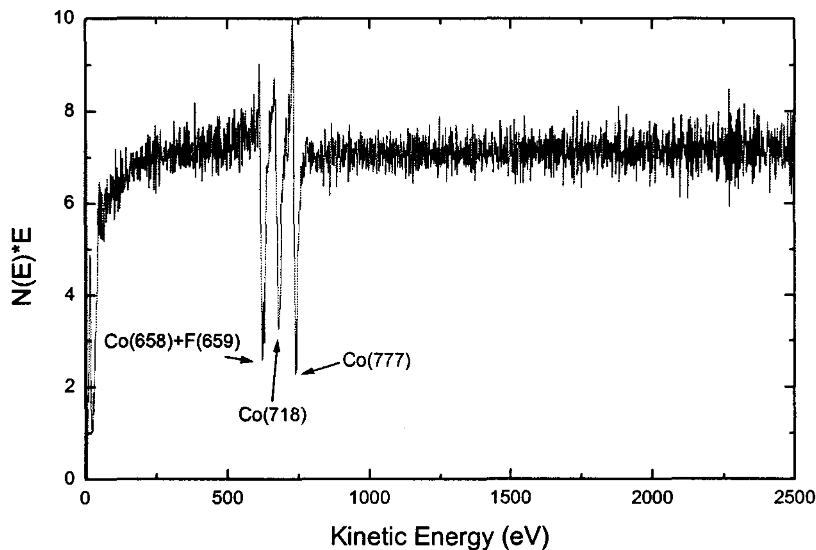


Figure 6. Three-dimensional AFM (Atomic Force Microscopy) image of SEM micrographs in Figure 5



(a) AES spectrum of intact metallic Co surface



(b) AES spectrum of reacted metallic Co surface

Figure 7. Differentiated AES spectrum of Co before and after etching reaction

Next, the intensities of the three Co peaks in Figure 7(b) must be carefully considered. It is noticeable that the intensity of the first peak at 658 eV is extraordinarily large compared with that in Figure 7(a). Careful scrutiny reveals that the 658 eV Auger electron binding energy peak of Co overlaps with the 659 eV F atom Auger electron peak, because the resolution of the spectrum is not less than 1 eV. Thus, this peak is unusually large. This implies that, given the extremely strong adsorption capability of fluorine atoms on the metallic surface being considered, most of the reacted cobalt metal surface is covered with the fluorine radicals generated in the incoming gaseous plasma and these adsorbed radicals must take a

leading part in the surface reaction.

Therefore, it can be mechanistically postulated that the adsorbed fluorine atoms interact with surface cobalt atoms and possibly carbon monoxide radicals abundantly generated in the plasma gas to form intermediate species, which are quite complex metal fluorides or metal-fluoro-carbonyl compounds that are ready to desorb from the surface. Further successive interactions with the incoming radicals from the gaseous plasma finally turn the metastable species into very volatile reaction products that then leave the surface. The surface is thus etched down.

IV. Conclusions

Both to demonstrate the practical applicability of the plasma surface cleaning technique and to promote the mechanistic understanding of the etching process, and to determine the optimum parameters, the decontamination rate of metallic cobalt is experimentally investigated via the surface-etching rate with CF_4 and O_2 mixed gas plasma. The selection of the target system is based on the fact that Co is one of the most troublesome radioactive contaminants in used nuclear metallic parts or equipment and the gas mixture plasma produces carbon monoxide (CO) and fluorine radicals (F) that are essential for the formation of the volatile gaseous reaction products.

Experimental results reveal that about $80\%CF_4$-$20\%O_2$ mixed etchant gas gives the highest reaction rate and the rate reaches 0.06 μm/min at 380 °C. This composition is also optimum at other substrate temperatures, even though the differences become less distinct as the temperature decreases. It is also found that there is almost no surface reaction at 290 °C. However, it begins to occur at around 350 °C and its rate increases sufficiently as the substrate temperature increases.

In this study, it is confirmed that ion-assisted etching dramatically enhances the surface reaction rate. Applying a 300 V DC bias to the substrate clearly lowers the surface reaction initiation temperature and dramatically increases the reaction rate. The rate increases about 20 times at 350 °C and the highest etching rate achieved at 380 °C jumps to 0.43 μm/min.

The changes in surface morphology as a result of the reaction confirm the etching rate measurements. According to SEM analysis performed after etching at 350 °C, the mirror-like flat surface of theintact metallic cobalt becomes rough with exposure to the reactive plasma gas and the negative bias voltage turns the moderate reaction into a vigorous one. In particular, the three dimensional AFM images vividly show the progressive roughness changes.

From the current experimental findings and the results discussed in previous studies, two prospective basic reactions, metal fluorination and/or metal carbonylation reaction, are proposed. To raise the mechanistic understanding of the principal surface reaction, however, the concentrations of surface atoms participating in the reaction are examined with AES analysis. The Auger spectrum shows evidence of the adsorption of fluorine atoms on the reacted surface.

Therefore, in view of the extremely strong adsorption capability of fluorine atoms on the metallic surface, it can be mechanistically postulated that most of the reacted cobalt metal

surface is covered with fluorine radicals. The adsorbed fluorine atoms interact with surface cobalt atoms and possibly carbon monoxide radicals generated in the plasma gas to form intermediate species, which are quite complex, but volatile, metal fluorides or metal-fluoro-carbonyl compounds. Further successive interactions with the incoming radicals from the gaseous plasma finally turn the intermediate compounds into very volatile reaction products that then leave the surface. The surface is thus etched down.

Through this study, it is ascertained that plasma surface-cleaning or surface-etching techniques can be efficiently and effectively applied tothe decontamination of spent or used nuclear parts and equipment if higher plasma power is used with the aid of ion-assisted etching techniques. In the near future, more thorough kinetic studies will be implemented in order to achieve a complete understanding of the surface-etching reaction.

References

1) OECD/NEA, Nuclear Decommissioning: Recycling and Reuse of Scrap Metals, A Report by a Task Group of the Co-operative Programme on the Decommissioning, OECD (1996).
2) IAEA, State of the Art Technology for Decontamination and Dismantling of Nuclear Facilities, Technical Reports Series No. 395 (1999).
3) INEL, Idaho National Engineering Laboratory Decontamination and Decommissioning Technology Logic Diagram", Vol. 3, EGG-WTD-11104 (1994).
4) T. Amakawa, K. Adachi, S. Yasui, and S. Furukawa, "Research and development of radioactive solid waste treatment technology by thermal plasma heating in CRIEPI", Proc. Plasma Processing for Nuclear Applications, Seoul, Korea, August 9 - 10 (2001).
5) I.N. Toumanov, Plasma and High Frequency Processes for Obtaining and Processing Materials in the Nuclear Fuel Cycle, Nova Science Publishers Inc. (2001).
6) C. Girold, B. Barthelemy, N. Cerqueira, C. Vandensteendam, and J.M. Baronnet, " Medium level burnable radioactive waste incineration/vitrification under oxygen transferred arc plasma", Proc. Intern. Symposium on Plasma Chemistry (ISPC) 15, Orleans, France, July 9 13 (2001).
7) Y.S. Kim, S.H. Jeon, and C.H. Jung, "Fluorination reaction of uranium dioxide in CF4/O2/N2 r.f. plasma", Annals of Nucl. Eng., 30, 1199 (2003).
8) Y.H. Kim, Y.H. Choi, J.H. Kim, J.K. Park, W.T. Ju, K.H. Paek, and Y.S. Hwang, "Decontamination of radioactive metal surface by atmospheric pressure ejected plasma source", Surface and Coatings Tech., 171, 317 (2003).
9) M. Suzuki, M. Komatsubara, M. Umebayashi, and H. Akatsuka, "Characteristics of microwave heated oxygen plasma and its application to oxygenation of metal chloride waste", Proc. Asia-Pacific Conference on Plasma Science & Technology, Tokyo, Japan, July 15 17 (1996).
10) Y.S. Kim, J.Y. Min, K.K. Bae, and M.S. Yang, "Uranium dioxide reaction in CF4/O2 rf plasma", J. Nucl. Mater., 270, 253 (1999).
11) K. Tatenuma, Y. Hishinuma, and S. Tomatsuri, "Newly developed decontamination

technology based on gaseous reactions converting to carbonyl and fluolic compounds", Nucl. Tech., 124, 147 (1998).

12) E.B. Munday and D.W. Simmons, Oak Ridge K-25 Site, K/TCD-1048 (1993).
13) J.G. Malm, P.G. Eller, and L.B. Asprey, "Low temperature synthesis of plutonium hexa-fluoride using di-oxygen di-fluoride", J. Am. Chem. Soc., 106, 2726 (1984).
14) W. Betteridge, Cobalt and Its Alloys, Halsted Press (1982).
15) J.C. Martz, D.W. Hess, J.M. Haschke, J.W. Ward, and B.F. Flamm, "Demonstration of plutonium etching in a CF4/O2 rf glow discharge", J. Nucl. Mater., 182, 277 (1991).
16) J.C. Bailar, H.J. Emeleus, S.R. Nyholm, and A.F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, Pergamon Press, New York (1973).
17) M.A. Lieberman and A.J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, John Wiley & Sons Inc. (1994).
18) D.M. Manos and D.L. Flamm, Plasma Etching, Academic Press Inc. (1989).
19) H.F. Winters, J.W. Coburn, and T.J. Chuang, "Surface processes in plasma-assisted etching environments", J. Vac. Sci. Tech. B, 1, 469 (1983).
20) F. Calderazzo, R. Ercoli, and G. Natta, Inorganic Synthesis via Metal Carbonyls I, Wender and P. Pino (Eds.), Interscience (1968).
21) K.D. Child, B.A. Carlson, L.A. LaVanier, J.F. Moulder, D.F. Paul, W.F. Stickle,and D.G. Watson, Handbook of Auger Electron Spectroscopy (3rd ed.), Physical Electronics Inc. (1995).