

Decontamination of Metal Surface by Reactive Cold Plasma

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SUMMARY

Recently plasma surface-cleaning or surface-etching techniques have been focused in the respect of decontamination of spent or used nuclear parts and equipment. In this study decontamination rate of metallic cobalt surface was experimentally investigated via its surface etching rate with a $\text{CF}_4\text{-O}_2$ mixed gas plasma and metallic surface wastes of cobalt oxides were simulated and decontaminated with $\text{NF}_3\text{-Ar}$ mixed gas plasma. Experimental results revealed that a mixed etchant gas with about 80% $\text{CF}_4\text{-}20\%\text{O}_2$ gives the highest reaction rate of cobalt disk and the rate reaches with a negative 300 DC bias voltage up to $0.43\ \mu\text{m}/\text{min}$ at $380\ ^\circ\text{C}$ and 20% $\text{NF}_3\text{-}80\%\text{Ar}$ mixed gas gives $0.2\ \mu\text{m}/\text{min}$ of reaction rate of cobalt oxide film.

Keywords: decontamination, cobalt-layer, plasma surface cleaning, ion-assisted etching

I. Introduction

Under continuous power operation, many major parts and equipment especially in the primary circuit of nuclear power plants are gradually surface contaminated by the absorption or adsorption of radioactive isotopes. Metal surface decontamination or etching techniques using reactive plasma gas is one of the emerging dry processing techniques applicable to surface contaminants with high bond energy, particularly for

the decontamination of spent or used nuclear parts and equipment. This technique can fulfill the requirement of minimum secondary waste generation while maintaining the same levels of efficiency as conventional wet decontamination techniques. In principle, the technique selectively picks up the surface contaminants, turns them into volatile compounds such as fluorides and/or carbonyl compounds through catalytic surface reactions, and finally evaporates them out of the surface. 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. 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. In this study, therefore, decontamination rate of cobalt metal was experimentally investigated via surface-etching rate with the focus on the mechanistic understanding of the reaction and the determination of optimum parameters.

II. Experimental

Experimental investigation on the cobalt surface etching rates was performed with two major experimental variables: volume ratio of O₂ to CF₄ in the binary etchant gas mixture and specimen substrate temperature. Then etching of cobalt oxide film on the stainless steel was followed.

As seen in Figure 2, plasma reactor was a diode type and rf power of up to 600 W could be applied between the parallel electrodes. Their distance could be adjusted, however, it was kept at 5 cm during entire measurements. Samples could be heated up to 800 °C by halogen lamps heater in the reaction chamber. The binary etchant gases, CF₄ and O₂, to cobalt disk and NF₃ and Ar to cobalt oxide film were supplied through mass flow controllers finely controlling their flow rates. Total gas pressure was maintained at 0.45

Torr in these measurements. Negative bias voltages could be applied as great as 500 V to the substrate but -300 V was chosen for the investigation.

Non-radioactive metallic cobalt with 99.8% purity was chosen as a specimen because it represents the real characteristics of cobalt elements than any other forms and does not require complicated radiation protection procedures. The metal piece was cut into thin disk specimens using a low-speed diamond wheel cutter. Prior to loading the sample to the reaction chamber, specimen surface was polished to a mirror-like finish with grit 600 sandpaper, pickled in a pickling solution ($\text{H}_2\text{O}:\text{HNO}_3:\text{HF} = 50:47:3$), cleaned ultrasonically, and baked at 200 °C for 10 minutes in a vacuum to evaporate moisture adsorbed on the surface. And to demonstrate the feasibility of plasma decontamination process, wastes of cobalt oxide form were simulated on the stainless steel. Cobalt nitrate solution was dropped on the stainless steel surface that has 2 mm of thickness and 10 mm of diameter and baked at 500 °C to make oxide film.

Decontamination rate was estimated as surface-etching rate translated from weight loss measurements during the reaction. The measurements were made with an electro-micro balance (model BP210D, Sartorius) with a sensitivity limit of 10^{-5} g and the weight loss is expressed in units of micrometers per minute.

Along with the decontamination rate measurements, OES (model SD 2000, Ocean Optics Inc.) and AES (model PHI680, Physical Electronics) analyses were carried out to diagnose plasma parameters and to obtain information on the reaction mechanism.

III. Results and Discussion

In order to find the highest reaction rate at given temperatures, etching rates were examined as a function of O_2 mole fraction at three substrate temperatures: 290 °C, 350 °C, and 380 °C. In the measurements, rf plasma power and exposure duration were

set to be 220 W and 120 minutes, respectively.

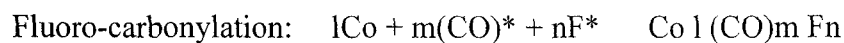
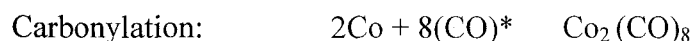
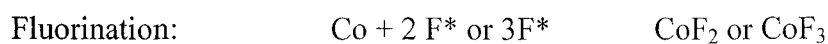
Figure 3(a) shows the results at 380 °C, revealing that about 80% CF₄ – 20% O₂ mixed binary gas gives the highest reaction rate and the rate reaches 0.06 μm/min. This optimum composition turned out to be invariant at other substrate temperatures as in the previous work, even though the effect becomes less distinctive at lower temperatures. In the mean time, OES plasma diagnostics result in Figure 3(b) shows that F and CO radicals are produced abundantly at around the optimum composition, demonstrating the significant role of fluorine and carbon monoxide radicals in the reaction. At this point, it is noticeable that the dependency of Co reaction on the O₂ fraction is quite sharp at the optimum composition while CO and F radical generation peaks are broad near the composition. This is comprehensible because they are completely different but related in terms of reactant radicals supply. Generation of the radicals results from homogeneous reaction (gas – gas interaction) in the gaseous plasma under the applied electrical energy and the produced radicals are in physical mixture state. On the other hand, surface reaction of metallic cobalt is a heterogeneous chemical reaction (gas – solid surface interaction) that requires an activation energy and stoichiometry. The heterogeneous reaction can be retarded by unbalanced stoichiometry or surface residuals for example, carbon residuals as discussed in the earlier work(7). Therefore, it can be suggested that the etching rate would be very low unless the peaks of the radical generation and the reaction rate locate at the same composition and so the reactant radicals are sufficiently supplied.

In the following measurements, it was found that the etching reaction hardly took place at 290 °C but began to occur at around 350 °C and its rate increased to 0.06 μm/min as the substrate temperature went up to 380 °C. These results are shown in Figure 4. Unfortunately, however, the etching rate attained at 380 °C was not high enough to be

useful for the practical decontamination. Therefore, in order to examine the reaction rate enhancement through the ion-assisted etching mechanism negative bias voltage was applied to the substrate of the metallic cobalt specimen and the etching rate measurements were repeated. Figure 4 clearly shows that the bias voltage lowers the surface reaction initiation temperature and increases the reaction rate substantially. With -300 V DC, the reaction became measurable even at 290 °C and progressed vigorously at 350 °C and its rate soared up to 0.43 $\mu\text{m}/\text{min}$. at 380 °C. This result proves that ion bombardments assist the surface reaction of the metallic cobalt. More specifically, the reactive ions generated in the plasma are accelerated towards the metal surface by the negative potential and their bombardments onto the surface impart their kinetic energy to the reaction-participating molecules, leading to drastic increase of reaction probability by lowering the activation energy for the surface reaction.

To confirm these results, surface morphology changes before and after the reaction were examined using SEM (model S-4700, Hitachi) and AFM (model SPA-400, Seiko Instrument). Figure 5 shows SEM micrographs taken before and after the reaction with/without substrate bias voltage at 350 °C. They evidently demonstrate that the mirror-like flat surface before the reaction became rough after the exposure to the reactive plasma gas and the application of the bias voltage turned the moderate reaction into a vigorous one. Figure 6 vividly presents three-dimensional AFM images of the micrograph showing the vigorous surface reaction.

Not only these experimental findings but also strong chemical reactivities of F and CO radicals, high volatility of fluoride compounds, and very low melting temperature of carbonyl compounds (Table 1) support that dominant surface reactions are fluorination and/or carbonylation. In fact, probable basic reactions are as follows:



To find the clues for the determination of the proposed reaction mechanisms, surface atoms analysis using AES was carried out before and after the reaction (Figure 7). Figure 7 a) shows AES spectrum of intact Co specimen, which is in good agreement with standard cobalt spectrum(20) except carbon and oxygen peaks. The carbon peak is from the residuals on the surface that always reside in vacuum systems. The two oxygen peaks must be from the thin oxide layer on the specimen surface. It is known that even after relatively thick oxide is removed in the pickling process a few mono-layers of thin oxide film inevitably form on the metal surface when the surface is exposed to the air because of high oxygen potential in the ambient environments(21-22). On the contrary, AES spectrum of the reacted surface plotted in Figure 7 b) shows only Co atom peaks without the carbon and oxygen peaks. Now, it is noteworthy that in the figure b) the intensity of first peak at 658 eV is extraordinarily large compared with that in the figure a). Careful scrutiny revealed that the 658 eV peak overlaps with 659 eV F atom Auger electron peak(20) because the resolution of the spectrum was about 1 eV. This implies that due to extremely strong adsorption capability of fluorine atoms on the metallic surface most of the cobalt metal surface is primarily covered with the fluorine radicals generated in the incoming gaseous plasma. This must be a partial reason that no oxide grows on the reacted surface, unlike the bare metal surface.

These AES results confirm that the adsorbed fluorine atoms must be involved and rather play significant roles in the surface reaction for the continuation of the reaction. This supports that sole carbonylation reaction is not possible. In the mean time, exclusive

fluorination reaction is not probable either because of their much higher melting points than the current reaction temperature. Therefore, only the cobalt fluoro-carbonylation reaction mechanism is plausible and thus proposed for the current cobalt surface etching system even though exact stoichiometry of the reaction is not certain yet at this stage. In fact, several papers have been published on the synthesis and characteristics of the metal carbonyl fluorides and have revealed their high volatility and low melting/decomposing temperatures(23-25). With the aid of these works the proposed mechanism can be described briefly in the following way. The adsorbed fluorine atoms interact with surface cobalt atoms and possibly carbon monoxide radicals abundantly generated in the plasma gas to form intermediate cobalt fluoro-carbonyl compounds. Further successive interactions with the incoming radicals from the gaseous plasma make them ready to desorb from the surface and finally turn the metastable species into very volatile reaction products. Then they immediately leave the cobalt metal surface so the surface is etched down.

In case with cobalt oxide film on stainless steel, It is easily stripped by NF_3 /Ar plasma with -300v negative bias voltage for 10 minute. That is confirmed by SEM image (Fig. 8). Through weight loss technique, reaction rate to remove cobalt oxide film is 0.2 $\mu\text{m}/\text{min}$.

IV. Conclusions

Decontamination rate of metallic cobalt was experimentally investigated via surface-etching rate with CF_4 - O_2 mixed gas plasma in order to demonstrate the practical applicability of plasma surface cleaning or etching process, to determine the optimum parameters of the process, and to promote the mechanistic understanding of the process. Experimental results revealed that about 80% CF_4 – 20% O_2 mixed etchant gas gives

the highest reaction rate and this optimum composition is invariant, regardless of substrate temperature. The results also showed that there was almost no surface reaction at 290 °C, however, it began to occur at around 350 °C and its rate increased to 0.06 µm/min. as the substrate temperature went up to 380 °C.

In the current study, it was found that ion-assisted etching lowers the surface reaction initiation temperature and substantially enhances the surface reaction rate of metallic cobalt. With -300 DC bias voltage applied to the substrate the reaction began to take place even at 290 °C and its rate increased significantly at 350 °C and soared up to 0.43 µm/min at 380 °C. Surface morphology changes revealed by SEM and AFM analysis also confirmed these etching rate measurements.

Based on the current experimental findings, surface atoms analysis using AES, and high volatilities of metal carbonyl fluorides, cobalt fluoro-carbonylation reaction mechanism is proposed for the current metallic cobalt surface etching system.

For cobalt oxide film, it is easily removed by NF₃/Ar plasma. and confirmed by SEM image. This result imply that contaminant which hardly adhered metal surface also easily decontaminated by reactive cold plasma.

Through this study, it is ascertained that plasma surface-cleaning or surface-etching techniques can be efficiently and effectively applied to the decontamination of spent or used nuclear parts and equipment with the aid of ion-assisted etching techniques. For complete understanding of the current surface-etching reaction mechanism, thorough kinetic studies will be followed.

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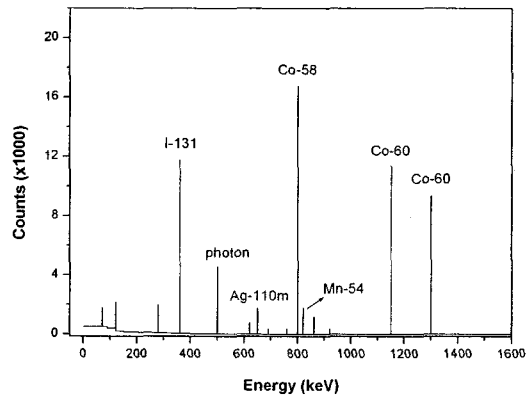


Figure 1. γ -spectroscopy results of discharged nuclear steam generator inconel alloy tube

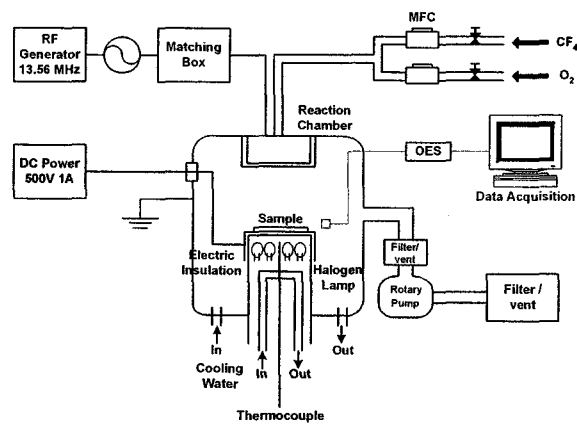
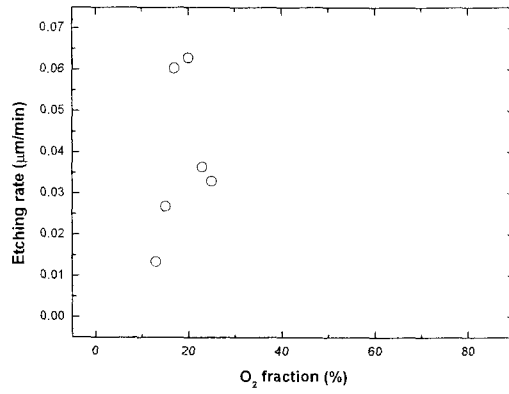
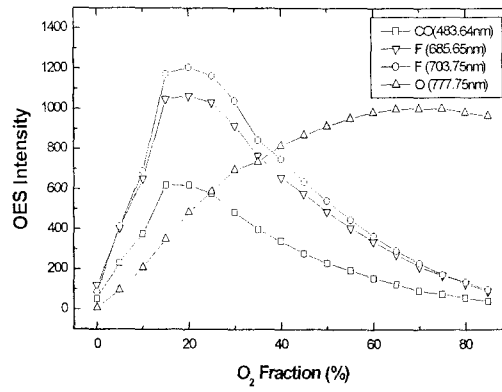


Figure 2. Schematic of cold plasma reactive ion etching apparatus.



(a)



(b)

Figure 3. (a) Co etching reaction rate vs. O₂ 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 O₂ mole fraction.

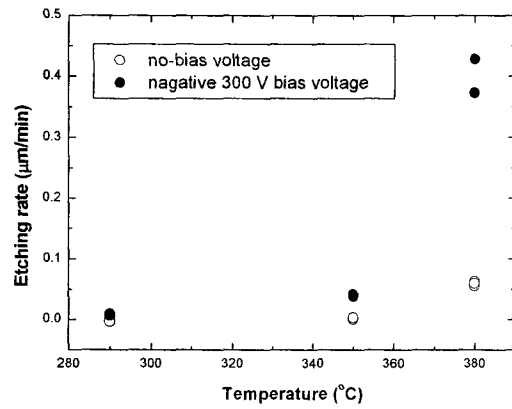


Figure 4. Co etching rate vs. various substrate temperatures

(total flow rate: 100 sccm, reaction time: 120 min., 20% O₂ mole fraction

rf power: 220 W, bias: -300 V, total pressure: 0.35 Torr)

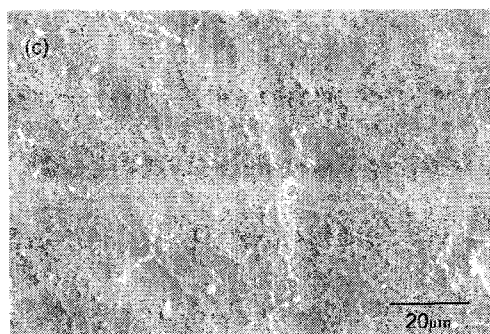
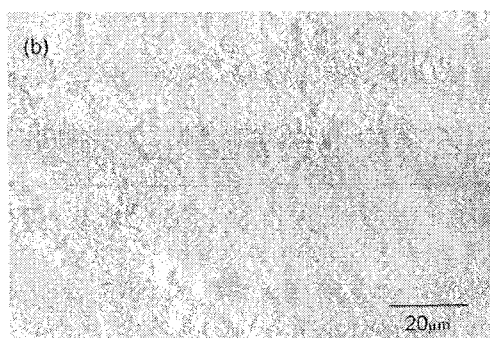
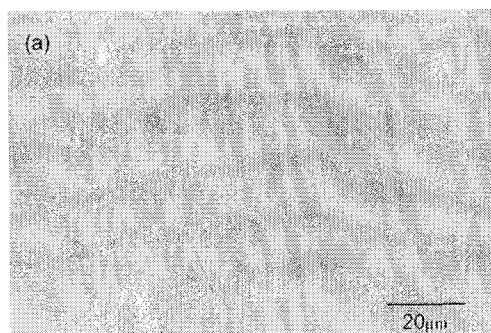


Figure 5. SEM micrographs of surface morphology changes

before and after surface reaction at 350 °C

(a) intact (b) no-bias voltage (c) -300 DC bias voltage

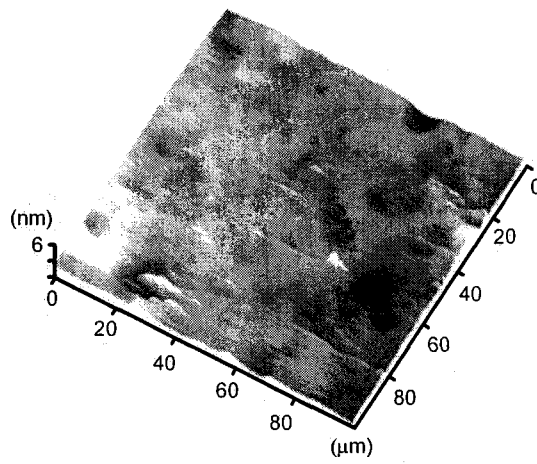
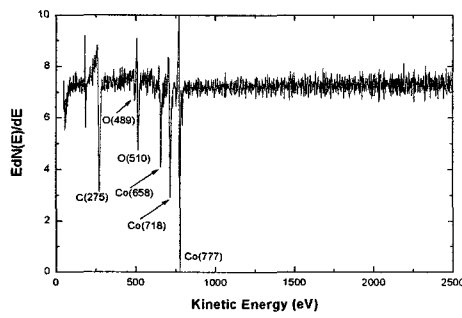
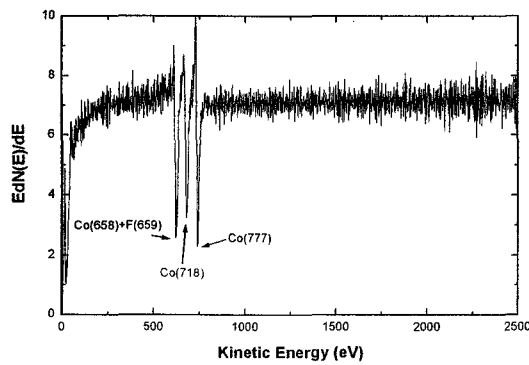


Figure 6. Three-dimensional AFM (Atomic Force Microscopy) image of SEM micrographs in Figure 5(c)

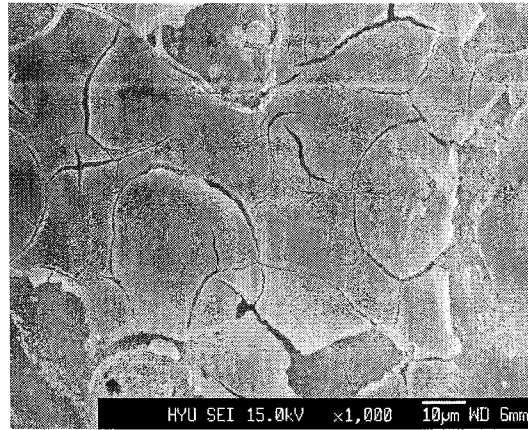


(a) AES spectrum of intact metallic Co surface

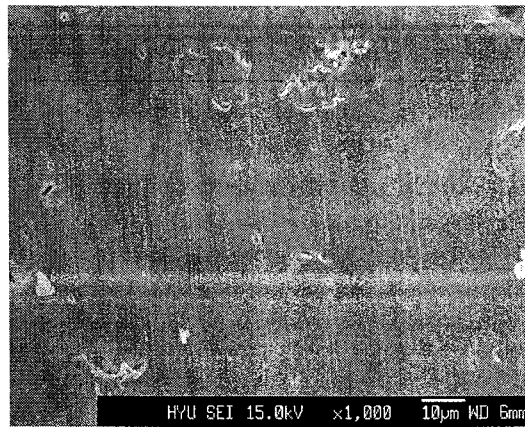


(b) AES spectrum of reacted metallic Co surface

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



(a) before etching



(b) after etching

Figure 8. SEM photograph of cobalt oxide film before and after etching reaction

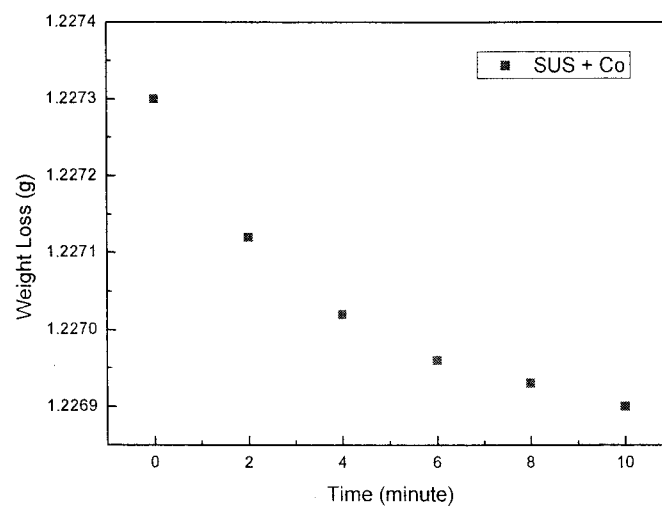


Figure 8. Etching rate of cobalt oxide film vs time