Surface Phenomena of Deuterized Ethanol Exposed Zircaloy-4 Surfaces

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We report the results of the surface chemistry of deuterized ethanol exposed Zircaloy-4 (Zry-4) surfaces with various amount of C$_2$D$_5$OD exposures at 190 K. This system was examined with Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) techniques. In TPD study, $D_2$ was evolved at two different desorption temperature regions accompanying with broad desorption background. The lower temperature feature at around 520 K showed first-order desorption kinetics. The high temperature desorption peak at around 650 K shifted to lower desorption temperature as the exposure of C$_2$D$_5$OD increased. The Zr(MNV) Auger peak shifted about 2.5 eV from 147 eV to lower electron energy followed by 300 L of C$_2$D$_5$OD dosing. This implies metallic zirconium was oxidized by deuterized ethanol adsorption. After stepwise annealing of the oxidized Zry-4 sample up to 843 K, the shifted Zr(MNV) peak was gradually shifted back to metallic zirconium peak position. After the sample was heated to 843 K, the oxygen content near the Zry-4 surface was recovered to clean surface level. The concentration of carbon, however, was not recovered by annealing the sample.

Key Words: Auger electron spectroscopy, Zircaloy-4, Ethanol, Temperature programmed desorption

Introduction

Due to the low thermal neutron capture cross-section, good corrosion resistance, and adequate mechanical properties, Zircaloy-4 (Zry-4) is often chosen as cladding tube materials in nuclear industry.\(^1\) Zry-4 contains 1.4 wt% Sn, 0.23 wt% Zr as the balance component. Zry-4 has been of great concern and investigated with a variety of surfaces in many fields. The corrosion,\(^3\) oxidation,\(^6\) and hydrogen absorption kinetics\(^18\) of Zry-4 and its nuclear application have been reported in literatures. Zry-4 oxidation by water (H$_2$O) and steam has been reported in many studies.\(^24\) Ramsier’s group reported that heating H$_2$O/Zry-4 surface resulted in molecular desorption of water at both low and high temperatures. Also they investigated that the behavior of water with sulfur dioxide pre-exposed Zry-4 surface.\(^27\) They studied that adsorption of SO$_2$ caused shift of the Zr(MNN) Auger electron feature by 3.0 eV, while subsequent water adsorption attenuated the sulfur Auger signal and resulted in the development of a zirconium oxide. The effects of adsorbates on the oxidation of Zry-4 in air and steam were studied by the measurement of the weight gain of specimens.\(^28\)

Reaction of alcohols on transition metal surfaces are of great interest. Ethanol has been receiving considerable attention recently because of its high potential for producing molecular hydrogen to power fuel cells.\(^33\) Ethanol is attractive due to its renewable nature since it can be produced in high yield by fermentation of crops. Because ethanol can be easily transported on board hydrogen generation by reforming is an attractive solution to feed fuel cells. Despite a few papers have studied about interaction of C$_2$D$_5$OD on zirconium, the surface chemistry of ethanol dosed on Zry-4 surface is not well known yet.

The Zry-4 sample used in this study has a thickness of 1.70 mm and surface area of 9.35 mm × 9.55 mm in a rectangular shape. It was prepared through many steps of polishing with different meshes of abrasive papers and mechanical polisher (Buehler, gamma alumina, 0.05 micron) for the final step of surface polishing. Then the polished Zry-4 was rinsed with acetone in ultrasonic cleaner for ten minutes. After the sample was rinsed with acetone and then the surface was blown with dry nitrogen gas. The prepared Zry-4 sample was mounted on the custom designed sample holder by spot welding on Ta wires. The type-K thermocouple was spot welded on the side of the Zry-4 for monitoring temperature. Before the experiment was performing, the sample was cleaned by many cycles of Ar$^+$ (99.999% purity, Aldrich) sputtering followed by annealing to 843 K. The Ar$^+$ sputtering process (IES 5, Omicron), the pressure of Ar$^+$ was kept at 1.5 × 10$^{-5}$ Torr for 1 hour in order to make 20 µA of a target current. And the Ar$^+$ fluence was 5.1 × 10$^{17}$ Ar$^+$cm$^{-2}$ per sputtering cycle. Cleanliness of the sample was confirmed by AES.

For TPD experiments, the sample was facing to the quadrupole mass spectrometer (QMS: Dycor Dymaxion, AMETEK) and the sample temperature was increased at a rate of 1 K/s by resistive heating using a feedback PID controller. The temperature of the sample was monitored by type-K thermocouple spot welded on the side of Zry-4 sample. The sample was cooled down by liquid nitrogen. When the temperature of the sample reached about 190 K, Zry-4 was exposed to the gas phase C$_2$D$_5$OD with various exposures. In order to identify the hydrogen produced from the ethanol not from the residual hydrogen the analysis chamber, high purity deuterized ethanol was introduced. The C$_2$D$_5$OD (99.95%, atom %) was purified through several times of freeze-pump-thaw (FPT) methods before introducing it into UHV chamber. The purity of C$_2$D$_5$OD after several cycles of FPT was checked by QMS. After the sample
was cooled down to 190 K, C$_2$D$_5$OD was backfilled into the main analysis chamber through a precision leak valve kept the pressure at 1.0 × 10$^{-6}$ Torr during gas dosing and the exposure time was measured until the pressure reached to 5.0 × 10$^{-9}$ Torr, then the sample was linearly heated up to 843 K. The possible desorption species from the deuterized ethanol adsorbed Zry-4 surfaces, such as H$_2$, HD, D$_2$, H$_2$O, D$_2$O, CO, and CD$_3$O were monitored applying multiple ion monitoring (MIM) mode in QMS.

The base pressure of UHV analysis chamber was kept at low 10$^{-10}$ Torr range. The details of the UHV analysis chamber are described elsewhere. The electron beam energy at 3 keV was used for retarding field AES (SpectaLEED 4-Grid, Omicron). The AES experiments were performed with 140 µA of a beam current, 0.3 mA of an emission current, 1.17 A of a filament current, and 75 µA of a target current. The current scan range for AES applied in this work was from 5 to 600 eV. The parameters for AES survey scan were 1 eV of an energy step, 3 mV of a lock-in sensitivity, and 100 ms of a lock-in time constant. The high resolution AE spectra were taken at the ranges for zirconium, carbon, and oxygen were from 70 to 180 eV, 240 to 300 eV, and 280 to 540 eV, respectively, with 0.2 eV of energy step and other factors were kept the same as survey scan. In AES study, sample temperature was raised stepwisely from 190 K up to 503, 628, 653, and 843 K then cooled down the sample to adsorption temperature for investigation of thermal effect on the C$_2$D$_5$OD/Zry-4 system. These temperatures were chosen in accordance to the results of TPD experiment. After sample was cooled down, AES data were collected.

**Results and Discussion**

Figures 1 (a) and (b) show the representative thermal desorption spectra of 2 amu (H$_2^+$ or D$_2^+$) and 4 amu (D$_2$), respectively, after different C$_2$D$_5$OD exposures at 190 K of adsorption temperature. The gas exposures are presented by langmuir unit (1 L = 1.0 × 10$^{-6}$ Torr s) unit. When the exposure of gas was lower than 50 L, no noticeable desorption was observed. Even ultra pure deuterized ethanol was used for this study hydrogen exchange could be occurred in the gas handling line. Because of the hydrogen exchange, H$_2$ desorption peak was detected. The hydrogen (2 amu) thermal desorption peak was observed at around 660 K at 53 L of ethanol exposure which increased in intensity with increasing C$_2$D$_5$OD exposure. The desorption peak temperature shifted to lower temperature according to the increase of gas exposure. This phenomenon could be explained by the second-order desorption kinetics. Especially, note the D$_2$ evolution (Figure 1 (b)), the desorption peaks appeared both ~520 K and ~650 K overlapped with broad desorption background from ~300 K to 750 K. This broad desorption background implies that complicate desorption kinetics was involving in D$_2$ desorption. The peak position of low temperature desorption feature (520 K) was constant with increasing the exposures of adsorbate indicating that the desorption of D$_2$ was the first-order desorption verified by peak-shape analysis. The high temperature desorption feature (660 K) gradually increased in intensity with exposure and shifted to lower temperature. It could indicate the second-order desorption kinetics.

The desorption feature of D$_2$ at low temperature was almost saturated at 53 L of C$_2$D$_5$OD exposure but the feature at high temperature was grown at the exposure increased (Fig. 1(b)). This could be explained that the low temperature feature was developed by the deuterium existed near the zircaloy-4 surface region which was easily saturated by 53 L of exposure and the other was evolved by the deuterium stayed in the bulk region. Higher exposure of C$_2$D$_5$OD, higher concentration of deuterium in the bulk is. The high temperature feature was only detected in H$_2$ desorption because the hydrogen existed in the bulk before C$_2$D$_5$OD exposure was desorbed (Fig. 1(a)).

Figure 2 shows the AES survey spectra of C$_2$D$_5$OD/Zry-4 system with various annealing temperatures. The intensity of Zr(MNV) Auger peak decreased after C$_2$D$_5$OD dosing on Zry-4 and then increased by annealing the sample as we expected. When the sample was annealed to higher tempera-

![Figure 1](image1.png)

**Figure 1.** Temperature programmed desorption spectra of (a) 2 amu and (b) 4 amu following C$_2$D$_5$OD adsorption on Zircaloy-4 at 190 K. The numbers in the figure represent the exposure in langmuir unit (L). The notations used in the title of these figures, such as H$_2$/C$_2$D$_5$OD/Zry-4, means H$_2$ evolution after C$_2$D$_5$OD dosed on the Zry-4 surfaces.

![Figure 2](image2.png)

**Figure 2.** Survey Auger electron spectra of the C$_2$D$_5$OD dosed Zry-4 surfaces.
The intensity of O(KLL) Auger peak decreased but that of C(KLL) increased. To study the details of the surface chemistry, high resolution AES experiments were carried out for the energy ranges of Zr (MNV), C (KLL), and O (KLL).

Figures 3 (a), (b), and (c) show the high resolution AE spectra of zirconium, carbon, and oxygen regions, respectively. We collected AE spectra after stepwise annealing of the sample to our interesting temperatures which were chosen considering with the TPD spectra shown in Figures 1, at and after the desorption peak maximum. The peak positions of Zr(MNV), C(KLL), and O(KLL) are assigned at the electron kinetic energy of 147, 270, and 510 eV, respectively. The vertical lines in the figures added for clarity. The intensity of Zr(MNV) feature was decreased after 300 L of C2D5OD exposure and gradually recovered by annealing as we expected. We should notice in Figure 3 (a) that the Zr(MNV) AE feature shifted to lower electron energy region (~2.5 eV) than the original peak position followed by C2D5OD dosing then shifted back to higher electron energy by increasing the temperature of annealing. This implies that the oxidation state of zirconium changed from metallic zirconium to zirconium oxide then back to nearly metallic zirconium by annealing. The change of zirconium oxidation state was supported by the AE spectra of oxygen (Figure 3 (c)) as well. As we can see in Figure 3 (c), the O(KLL) peak was increased by 300 L of C2D5OD exposure. Then the intensity of O(KLL) was decreased by annealing to the level before dosing of C2D5OD. The Auger electron intensity of C(KLL) stayed almost constant until the sample temperature reached to 628 K shown in Figure 3 (b). After this temperature C(KLL) intensity increased by annealing. This could be happened that the defragmented carbon in subsurface region was diffused out after the constituents near the surface were desorbed out to vacuum by annealing. These carbon diffused from the subsurface region was not cleaned before 10 cycles of Ar sputtering process. We should notice that the line shape of C(KLL) shown in Figure 3 (b). The line shape of C(KLL) feature, i.e. oscillation of peak at low kinetic energy side, could be used to differentiate carbide and graphitic carbon reported by Gomer’s group. The peak oscillation of low kinetic energy region of C(KLL) was diminished when the sample was annealed to 503 K, then the oscillation was recovered with further annealing the sample to 843 K. This implies that the dominant carbon state of the C2D5OD/Zr-4 changed from carbide through graphitic to carbide carbon on the surface by annealing. Tanaka et al. have reported the formation of hybrid surface of carbide and graphite layers at 630-640 K on Ni surface by disproportionation reaction of CO. Further study needs to verify the carbon state by work function measurement for this system.

Figure 4 shows the Auger peak-to-peak heights (APPH) ratios of C(KLL)/Zr(MNV) and O(KLL)/Zr(MNV). The APPH ratios of C/Zr and O/Zr are 1.91 and 0.62, respectively for the clean surface. The APPH ratios are calculated concerning with Auger sensitivity factors of the elements. The both ratios are increased after 300 L of deuterized ethanol dosing, and nearly stayed in constant level until the sample was heated to 628 K. When the sample was heated over 653 K, the ratio of C/Zr increased gradually but that of O/Zr decreased nearly back to the clean surface level. The carbon diffused onto the surface region by heating formed carbide form with zirconium, because of its small diffusion coefficient. The diffused out surface oxygen with large diffusion coefficient could be diffused into the bulk caused relatively lower surface contents of oxygen than that of carbon. These phenomena is consistent with the observation reported by other group.

Conclusions

The surface chemistry of C2D5OD on Zry-4 surface was investigated using AES and TPD methods. Isotopic hydrogen was detected from deuterized ethanol dosed Zry-4 surfaces at two different desorption temperature regions accompanying with broad desorption background. This shows the possibility of using hydrocarbon derivatives for the source of hydrogen used in fuel cell. The lower temperature feature at around 520 K stayed the same temperature increasing C2D5OD exposure.
This implies D\textsubscript{2} desorption is first-order desorption kinetics. The TPD peak of D\textsubscript{2} at around 650 K was shifted to lower desorption temperature as the exposure of C\textsubscript{2}D\textsubscript{5}OD increased. In AES study, the Zr(MNV) Auger peak was shifted about 2.5 eV from 147 eV to lower electron energy followed by 300 L of C\textsubscript{2}D\textsubscript{5}OD dosed. This implies metallic zirconium was oxidized by deuterized ethanol adsorption then reduced back to metallic zirconium by annealing because the oxygen near the surface was depopulated by heat treatment.

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References