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Surface oxidation of Zircaloy-4 at 600 K by adsorbed oxygen, nitric oxide, and sulfur dioxide

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Abstract

Understanding and controlling the formation of surface oxides on Zircaloy-4 (Zry-4) surfaces in the presence of nitrogen or sulfur at high temperatures is of interest in applications where this alloy serves as a structural material. In this article we monitor the adsorption of gases on Zry-4 surfaces at 600 K using Auger electron spectroscopy. We find that sulfur dioxide (SO_2), nitric oxide (NO), and isotopic oxygen ($^{18}O_2$) all result in the formation of surface oxides. The presence of sulfur on the surface is reflected both in an increase in the intensity of the overlapping [Zr(MNV) + S(LMM)] feature and its shift toward higher kinetic energies. On the other hand, since oxide formation results in shifts of the Zr(MNV) Auger transition toward lower energies, opposite to what the presence of sulfur does, we also obtain useful information from the Zr(MNN) transition. Although exposure to oxygen results in the largest oxygen concentration near the surface, all the three adsorbates shift the Zr(MNN) feature by about 1.5–2.0 eV, indicative of surface oxidation.

1. Introduction

Very few ultra-high vacuum studies of the influence of sulfur on zirconium surface chemistry exist in the literature. In a study by Tanabe and Tomita, delayed surface oxidation of zirconium was reported on sulfur-segregated polycrystalline zirconium [1]. The effect of sulfur on oxygen adsorption on polycrystalline zirconium surfaces below 315 K was studied by Ojima and Ueda, who reported a significant decrease in the oxygen sticking coefficient on sulfur-contaminated Zr surfaces [2]. In a room-temperature study of H_2S/Zr(0001), Wong and Mitchell reported that surfaces with high sulfur concentration did not adsorb oxygen in detectible amounts [3]. On the other hand, we investigated the interaction of SO_2 with Zr(0001) at 150 K [4], and recently with Zry-4 at various temperatures (300, 600, and 900 K) [5]. Interestingly, we found that under similar exposure conditions, the greatest amount of sulfur resides in the near-surface region following 600 K adsorption.

More attention has been given to investigating the interaction of nitrogen-containing species with zirconium surfaces. For example, the behavior of

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ammonia on Zr(0001) surfaces following low-temperature adsorption has been investigated in our laboratories, and complicated desorption kinetics were observed [6,7]. Foord et al. reported that nitrogen dissociates at room temperature on polycrystalline zirconium and then forms an underlayer structure [8]. Wong and Mitchell investigated the Zr(0001)–(1 × 1)-N surface structure following adsorption of nitrogen gas at room temperature [9]. Using low-energy electron diffraction (LEED) intensity analysis, they reported that N atoms may occupy octahedral sites between the first and second metal layers. A theoretical study based on first-principles total-energy and force calculations of nitrogen chemisorption on Zr(0001) surfaces revealed that subsurface octahedral sites are energetically more favorable for nitrogen adsorption than surface sites [10]. Furthermore, the adsorption of nitric oxide on Zr(0001) at low-temperatures (170 and 180 K) was investigated in our laboratories [11], and surface oxidation was observed using Auger electron spectroscopy (AES). Even though studies of the interaction of nitric oxide with polycrystalline zirconium at room temperature [8] are also available, it remains to be determined how the interaction proceeds at higher temperatures.

Oxygen is one of the most frequently studied species on zirconium surfaces, although surface science studies are typically conducted at room temperature or below [12]. In a room temperature study of oxygen adsorption on polycrystalline zirconium surfaces, Kurahashi and Yamauchi observed the appearance of a ZrO_2 phase in the top surface layer at exposures of about two Langmuir ($L = 10^{-6}$ Torr s) that dominated above 8 L [13]. The authors suggested a coexistence of two phases in 2–8 L range, ZrO_2 and a 'subsurface oxygen' phase. Zhang et al. investigated the initial oxidation of Zr(0001) up to 0.5 monolayers and reported that a large fraction of oxygen (70–75%) absorbs directly into subsurface sites even at temperatures as low as 90 K [14]. Following oxygen adsorption at 473 K, all oxygen atoms reside in subsurface sites. The authors also reported that the subsurface layer is stable against further diffusion into the bulk up to about 573 K.

Based on an initial decrease in work function upon oxygen adsorption at 82 K, Griffiths proposed the incorporation of oxygen into subsurface sites [15]. At low coverages LEED crystallographic analysis supports the occupation of subsurface sites [16]. First-principles total-energy calculations based on density functional theory showed that for coverages up to one monolayer, oxygen favors subsurface sites on Zr(0001) [17]. Yamamoto et al. also showed that for the O/Zr(0001) system oxygen favors octahedral sites between the second and the third metal layers in Zr(0001)–(1 × 1)-O and (2 × 1)-O structures [18].

Although there is a significant amount of research performed on zirconium surface chemistry [12], there are many open questions concerning processes at temperatures relevant to nuclear applications. At present, it is not clear how impurities such as sulfur or nitrogen affect the formation of oxide layers at high temperatures. These are relevant issues due to the gettering nature of zirconium for O and N and sulfur segregation from the bulk to the near-surface region at high temperatures [19]. Here, we investigate the adsorption of oxygen-containing molecules, in particular SO_2, NO, and $^{18}O_2$, on Zry-4 surfaces at a temperature relevant to nuclear applications (600 K). We conduct high-temperature AES experiments [19] under ultra-high vacuum conditions and monitor surface oxidation focusing on the Zr(MNN) Auger transition and exposures up to 35.0×10^{14} molecules/cm^2.

2. Experimental details

Experiments were conducted in a stainless-steel ultra-high vacuum chamber [20] with exposure to gases performed via a molecular beam doser [21] with the sample temperature maintained at 600 K. We have previously shown that high-temperature annealing has little effect on Auger spectra [19]. The Zry-4 sample has a thickness of 0.2 cm and a surface area of 0.5 cm^2. Its elemental composition, in wt%, is nominally 1.2–1.4% Sn, 0.2% Fe, 0.2% Cr + O + Si, and the balance Zr. The surface was cleaned by 3 keV Ar-ion sputtering below room temperature followed by annealing to 920 K at a heating rate of 1.8 K/s. The cleanliness of the surface was verified using retarding field Auger electron spectroscopy (AES) with a 3 keV beam energy. After our cleaning procedure, both the C(KLL)/Zr(MNN) and O(KLL)/Zr(MNN) ratios are less than 0.10. Tin, whose Auger signal is notably more intense than that of the minor alloying elements, never produced a Sn(MNN)/Zr(MNN) ratio greater than 0.12 [19].

For adsorption experiments we used isotopic oxygen ($^{18}O_2$, 99%, Matheson), nitric oxide (NO, 99%, Matheson), and sulfur dioxide (SO_2, 99.98%, Matheson). Exposures are presented as the number of molecules per cm^2. Prior to each gas exposure, the gas-handling manifold was pumped with a turbomolecular pump. The sample is cooled using a Cu braid connected to a liquid N_2 cold finger, whereas for resistive heating Ta wires, spot-welded to the sides of the sample, are used.

3. Results and discussion

Survey AES scans of Zry-4 surfaces exposed at 600 K to sulfur dioxide, nitric oxide, and oxygen are shown in Fig. 1. Exposures for this data set are in the range $27–30 \times 10^{14}$ molecules/cm^2. Note that signal intensities in panels (B) and (C) are on a scale four times more sensitive than that of panel (A). Panel (A) reveals the presence of sulfur, reflected in the large [Zr(MNV) + S(LMM)] Auger peak-to-peak signal, and oxygen, as indicated by the O(KLL) transition. Panel (B) clearly indicates that following adsorption of NO both nitrogen and oxygen reside in the near-surface region of Zry-4, whereas panel (C) shows that following adsorption of $^{18}O_2$, the oxygen signal dominates.

Our cleaned surface has a [Zr(MNV) + S(LMM)]/Zr(MNN) Auger peak-to-peak height ratio in the range 1.1–1.3 that corresponds to sulfur-free zirconium according to other research groups [3,8,22]. After adsorption of sulfur dioxide (27.2×10^{14} molecules/cm^2) at 600 K this ratio increases to 8.0 (Fig. 1(A)). However, due to the overlap of the Zr(MNV) and S(LMM) Auger transitions it is difficult to determine the exact amount of sulfur in the near-surface region. Note that the presence of sulfur makes the surface appear cleaner with respect to other impurities such as O and C. In an earlier study, we investigated sulfur segregation during annealing at high temperatures and found that after 180 min of annealing at 1012 K, this ratio was slightly below 4.0. We also addressed the issue of the presence of sulfur contamination on the apparent cleanliness (based on AES) of zirconium surfaces [19].

Following adsorption of NO on Zry-4 at 600 K, the presence of nitrogen and oxygen near the surface (Fig. 1(B)) results in the attenuation of zirconium Auger electrons. The Zr(MNV) feature that involves valence electrons is more affected than the Zr(MNN) transition, consistent with results from the work by Foord et al. [8]. Following adsorption of 30.0×10^{14} NO molecules/cm^2 the [Zr(MNV) + S(LMM)]/Zr(MNN) ratio is reduced to 0.7. The same exposure to oxygen (Fig. 1(C)) results in a sig-

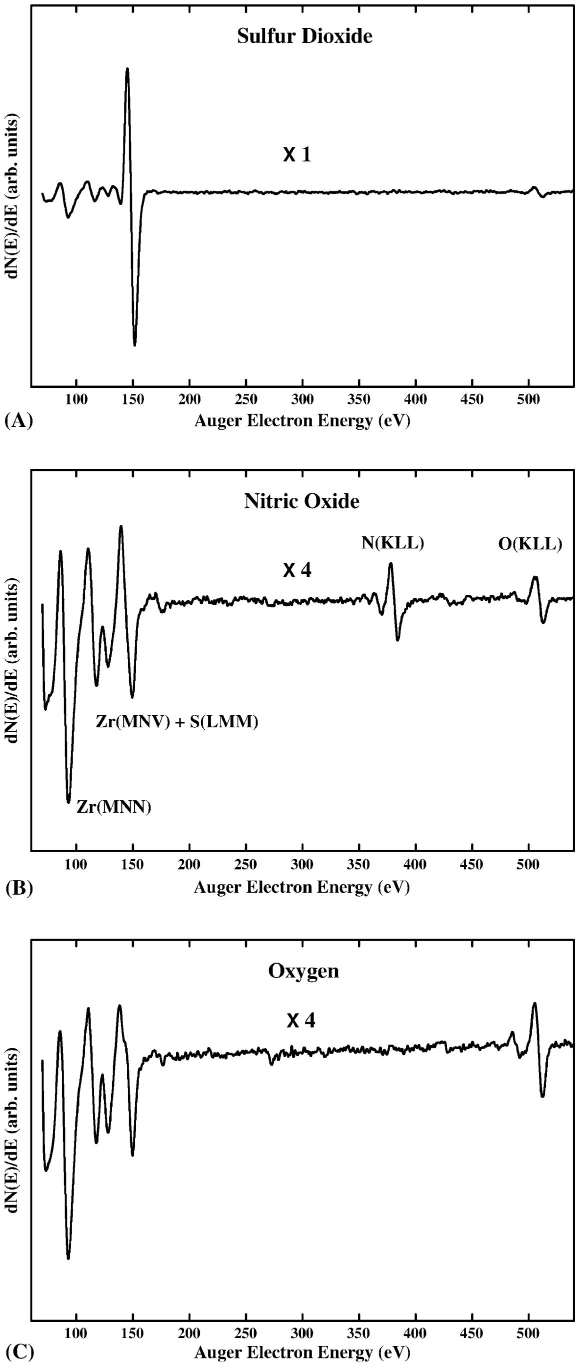

Fig. 1. Derivative mode AES of a Zry-4 surface exposed to sulfur dioxide (A), nitric oxide (B), and oxygen (C) at 600 K. The main Auger transitions are indicated in panel (B) for clarity. It should be noted that sulfur is only present in significant quantities in panel (A), where the S(LMM) feature dominates the Zr(MNV) and the intensity of the feature near 150 eV is relatively large. In panels (B) and (C), the features near 150 eV are representative of Zr(MNV) transitions only.

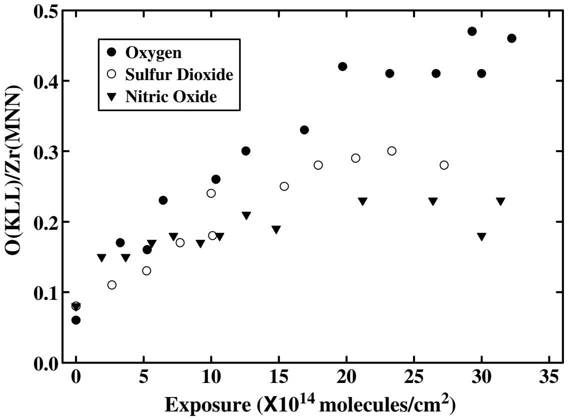

Fig. 2. The O(KLL)/Zr(MNN) Auger peak-to-peak height ratio as a function of exposure following adsorption of sulfur dioxide, nitric oxide, and oxygen at 600 K.

nificantly greater O(KLL) Auger signal since the near surface sites are occupied by oxygen atoms only, however the [Zr(MNV) + S(LMM)]/Zr(MNN) ratio is also 0.7.

Fig. 2 shows the O(KLL)/Zr(MNN) ratio as a function of exposure at 600 K for all the three adsorbates. The normalization with respect to the Zr(MNN) feature is commonly used in the literature since it is less affected by chemisorption than the Zr(MNV) transition as mentioned above [8]. As expected, the greatest oxygen signal is observed following adsorption of oxygen. Following adsorption of sulfur dioxide and nitric oxide, sulfur and nitrogen compete for near-surface sites resulting in a reduction in the oxygen Auger signature. It is interesting that after SO_2 adsorption, slightly more oxygen resides near the surface than after NO adsorption, especially when one considers previously reported effects of sulfur on oxygen interactions with zirconium. This implies that the competitions for surface and subsurface sites between sulfur and oxygen, and between nitrogen and oxygen, are complex. Both experimental and theoretical studies indicate that oxygen and nitrogen favor subsurface sites at low coverages. On the other hand, Ojima and Ueda reported that sulfur segregates at higher temperatures to occupy the hollow or the on-top sites [2]. Most likely in our experiments more oxygen resides beneath nitrogen in the NO/Zry-4 system than beneath sulfur for the SO_2/Zry-4.

It is noteworthy that Hoflund et al. studied the interaction of gases with polycrystalline zirconium at room temperature using AES and presented some interesting results following CO adsorption [23]. Namely, using ion scattering spectroscopy they observed an oxide layer with no C whereas AES showed the presence of carbon beneath the oxide layer. In our experiments we are unable to determine whether sulfur and nitrogen reside beneath the oxide layer since AES probes more than just the outermost atomic layer.

It is also interesting to mention that in a study of $^{18}O_2$ adsorption on Zry-4 at 150 and 300 K in a wide exposure range we observed no difference in the amount of oxygen residing near the surface [24]. In the present study, we observe that oxygen exposures at 600 K up to 35.0×10^{14} molecules/cm^2 leave similar amounts of oxygen near the surface as compared to oxygen adsorption at 150 and 300 K [24]. Foord et al. studied the interaction of NO and O_2 with polycrystalline zirconium at 300 K and reported almost complete dissociation [8]. Saturation exposures were estimated to be 30 L for O_2 (1.1×10^{16}/cm^2) and 20 L for NO (0.7×10^{16}/cm^2). The same initial sticking probability of O_2 and NO were reported, as were similar attenuation factors for zirconium Auger features. Foord et al. also reported that the Zr(MNN) transition that we highlight in Fig. 3(A) was least affected by chemisorption.

Fig. 3 shows Auger spectra of zirconium and sulfur (A) and oxygen (B) features of a cleaned Zry-4 surface, and after exposure, 10.0×10^{14} molecules/cm^2 of SO_2, NO, and $^{18}O_2$ at 600 K. A vertical line on the Zr(MNN) transition is inserted to emphasize the change in the oxidation state of zirconium following exposure. Note that in all the three cases the Zr(MNN) transition shifts by 1.5–2.0 eV with respect to the clean-surface value. Higher exposures to SO_2, NO or $^{18}O_2$ up to 35.0×10^{14} molecules/cm^2 do not shift the Zr(MNN) feature further within an uncertainty of 0.5 eV. This is interesting since the adsorption of oxygen results in the greatest O(KLL), as shown in panel (B). The presence of sulfur that is known to delay surface oxidation [1], and the presence of nitrogen that competes for near-surface sites with oxygen, have little effect on oxidation at 600 K. Also note in panel (A) that, in addition to an increase in the [Zr(MNV) + S(LMM)]/Zr(MNN) feature, the presence of sulfur is also reflected in a shift of the minimum of the overlapping Auger feature toward higher energies. This shift was also observed in a study by Ojima and Ueda [2].

We are also interested in comparing our results on Zry-4 with those on single crystals and polycrystalline zirconium surfaces at various adsorption

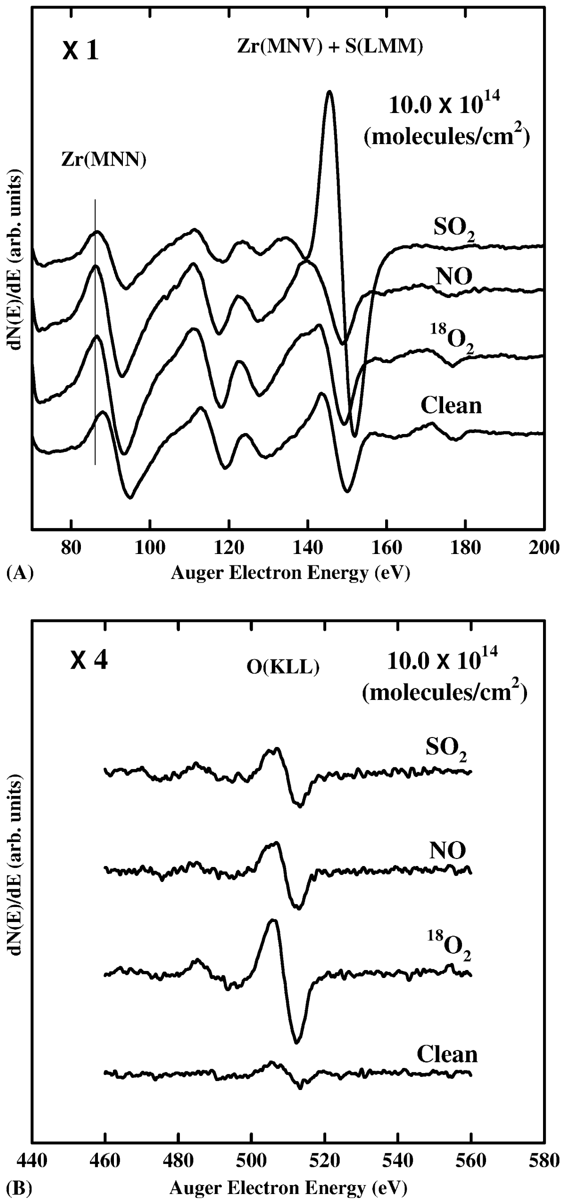

Fig. 3. Auger electron spectra showing zirconium and sulfur (A), and oxygen (B) features following exposure of Zry-4 to 10.0×10^{14} molecules/cm^2 of sulfur dioxide, nitric oxide, and oxygen. In all the three cases, the Zr(MNN) feature shifts by 1.5–2.0 eV. The vertical line is inserted to emphasize the change in the oxidation state of zirconium.

temperatures. It is important to mention that we observed that saturation oxygen adsorption on Zry-4 at 150 and 300 K resulted in the shift of the Zr(MNN) feature by 3 eV at both temperatures. In our recent study of SO$_2$ adsorption at 300 K, a shift in the Zr(MNN) transition of about 3 eV was also observed. Comparing to what we present here, we conclude that adsorption temperature has a significant effect on surface oxidation and that stronger oxidation occurs at lower temperatures for the same exposures. It was reported that at lower temperatures some oxygen resides at the surface of Zr(0001) whereas at temperatures above 473 K all oxygen is in the subsurface region [14]. Normally at higher temperatures reactions such as oxidation occur more rapidly, whereas here, the dissolution of adsorbates into the substrate at higher temperatures has a significant effect. It is therefore likely that in our experiments at lower temperatures more oxygen resides at the surface, thus enhancing surface oxidation. Adsorption at 600 K consists of the dissociation of chemisorbed molecules and the penetration of their fragments into the subsurface sites even at low exposures. This interpretation is consistent with the findings of related studies [14,25,26].

4. Concluding remarks

Understanding and controlling the surface chemistry of Zry-4, in particular the formation of surface oxides above room temperature on surfaces containing nitrogen or sulfur, is of interest in applications where this alloy serves as a structural material. The relevance of studying sulfur- and nitrogen-containing species like SO$_2$ and NO is that sulfur or nitrogen may segregate to alloy surfaces at high temperatures, or be present as contaminants in the coolant, and thus affect waterside corrosion. Since our experiments are short in duration with respect to the time-scales that Zry-4 components are used in service, we deliberately introduce these impurities from the gas phase rather than wait for outward migration at 600 K. Our main interest here was to compare the effects of S and N on surface oxidation at 600 K. Since the Zr(MNV) and S(LMM) Auger transitions overlap, monitoring shifts in the position of the Zr(MNN) peak is a useful way of observing surface oxidation. We found that the presence of sulfur (from SO$_2$) and nitrogen (from NO) does not affect the surface oxidation state significantly. For a related study on the effect of pre-adsorbed sulfur on the adsorption and desorption of water, the reader is referred to Ref. [27].

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