

Adsorption of water on sulfur dioxide pre-exposed Zircaloy-4 surfaces

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Received 10 October 2005; Revised 21 November 2005; Accepted 21 November 2005

We investigate the interaction of water (H₂O) with sulfur dioxide (SO₂) pre-exposed Zircaloy-4 (Zry-4) surfaces. Adsorption of SO₂ shifts the Zr(MNN) Auger electron feature by 3.0 eV, whereas subsequent water adsorption attenuates the sulfur Auger signal and results in the development of a zirconium oxide, Zr(MNV)_o, feature. No further shift in the Zr(MNN) transition is observed with increasing H₂O exposures. Following higher H₂O exposures on SO₂-saturated Zry-4 surfaces, linear heating results in water desorption near 500 K. This temperature is more than 200 K lower than the desorption temperature of water from clean Zry-4 surfaces. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: water; sulfur dioxide; Zircaloy-4; AES; TPD

INTRODUCTION

The behavior of water on zirconium surfaces is well documented in the literature.¹ The interaction of water with Zircaloy-4 (Zry-4) and Zr surfaces at low temperatures has been recently investigated using Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) methods.^{2,3} It was observed that at high exposures water shifts the Zr(MNN) feature by 4.5 eV. It was also found that molecular desorption occurs at both low and high temperatures. Low-temperature desorption was assigned to multilayer desorption, whereas the high-temperature desorption features, presumably owing to recombinative processes, also showed some characteristics of zero order kinetics. In this paper, we are interested in the effect of sulfur and oxygen from dissociated SO₂ on the subsequent adsorption and desorption of H₂O. Since sulfur and oxygen are difficult to remove from the near-surface region of zirconium-based materials and since Zry-4 serves as a structural component directly exposed to water in nuclear reactors, this study is of fundamental as well as applied interest.

EXPERIMENTAL

AES and TPD experiments were conducted in a stainless steel ultra-high vacuum chamber⁴ with a base pressure of approximately 3×10^{-10} Torr. Exposure to water vapor was performed via a molecular beam doser.⁵ The Zry-4 sample had a thickness of 0.2 cm and a surface area of 0.5 cm², with an elemental composition that is nominally expressed in wt%, 1.2–1.4% Sn, 0.2% Fe, 0.2% Cr + O + Si with the

balance Zr. We used 2 keV Ar-ion sputtering followed by annealing to 920 K with a heating rate of 1.8 K/s to clean the surface, and the cleanliness of the surface was verified using retarding field AES at 3 keV beam energy. After cleaning, the C(KLL)/Zr(MNN) and O(KLL)/Zr(MNN) Auger peak-to-peak height ratios were less than 0.10. Tin, whose Auger signal was notably greater than that of other alloying elements, did not exhibit a Sn(MNN)/Zr(MNN) ratio larger than 0.12. Zr-based materials are difficult to clean since complete removal of oxygen and carbon results in sulfur segregation to the surface. Following heating to 900 K, oxygen is completely removed from the surface, whereas sulfur remains. Repeated AES scans did not reveal any effects of electron beam heating or electron-stimulated desorption⁶ in our experiments, but we cannot rule out effects of electron beam damage that might occur in short time intervals. The sample current density during AES was about 15 $\mu\text{A}/\text{cm}^2$.

For water adsorption experiments, vapor from deionized water was used. Adsorption of water was performed at 150 K, whereas exposure to sulfur dioxide was conducted at 300 K. We are primarily interested in investigating the effects of residual sulfur and oxygen on the high-temperature desorption of water that occurs following low-temperature adsorption.² Preliminary results show very little water desorption following relatively high exposures to water at 300 K, and hence, we performed exposure to H₂O at 150 K. Exposure to water at 300 K oxidizes the surface, and does not produce much water in TPD but instead the oxygen dissolves into the subsurface region during heating. We also observe multilayer desorption after higher exposures at 150 K. Prior to each gas exposure the gas-handling manifold was pumped with a turbomolecular pump. The sample was cooled using a Cu braid connected to a liquid N₂ cold finger, whereas for resistive heating, Ta wires, spot-welded to sample sides, were used.

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RESULTS AND DISCUSSION

Figure 1 shows the $[\text{Zr}(\text{MNV})_m + \text{S}(\text{LMM})]/\text{Zr}(\text{MNN})$ and $\text{O}(\text{KLL})/\text{Zr}(\text{MNN})$ Auger peak-to-peak height ratios following SO_2 adsorption on Zry-4 at 300 K. The $\text{Zr}(\text{MNV})_m$ transition corresponds to metallic zirconium, following the notation used by other groups.^{7,8} Auger signals of sulfur and oxygen appear to saturate at exposures of about $10.0 \times 10^{14}/\text{cm}^2$. Saturation with SO_2 at relatively low exposures is consistent with what we observed previously for the $\text{SO}_2/\text{Zr}(0001)$ system.⁹ It is interesting that in our recent study of SO_2 adsorption on Zry-4 at various temperatures, we observed that more sulfur, and less oxygen, reside near the surface at 600 K than following adsorption at 300 K.¹⁰ This implies that sulfur and oxygen compete for the near-surface sites and that the outcome depends on adsorption temperature. Presumably, this competition is kinetically rather than thermodynamically controlled.

The presence of sulfur on zirconium surfaces is known to affect the surface chemistry of zirconium.^{11–13} Tanabe and Tomita investigated the effects of surface sulfur on the oxidation of polycrystalline zirconium and reported delayed surface oxidation.¹¹ In a related study, Ojima and Ueda observed that S-segregated surfaces had significantly reduced sticking coefficients for oxygen.¹² Interestingly, in a study of the adsorption of O_2 and H_2S on $\text{Zr}(0001)$, Wong and Mitchell observed that surfaces with high sulfur coverage did not adsorb oxygen in detectable amounts.¹³ We investigated the interaction of SO_2 with $\text{Zr}(0001)$ at 150 K and found that surfaces saturated with sulfur dioxide at exposures of about 1 l ($1 = 10^{-6}$ Torr s).⁹ In a recent study of SO_2 adsorption on Zry-4, we observed that higher exposures to SO_2 at 300 K result in a shift of the $\text{Zr}(\text{MNN})$ transition by 3.0 eV, indicating surface oxidation.¹⁰ Even though the effect of sulfur on oxygen adsorption has been documented in the past,^{11–13} how the presence of sulfur affects water adsorption and desorption has, to our knowledge, not been investigated.

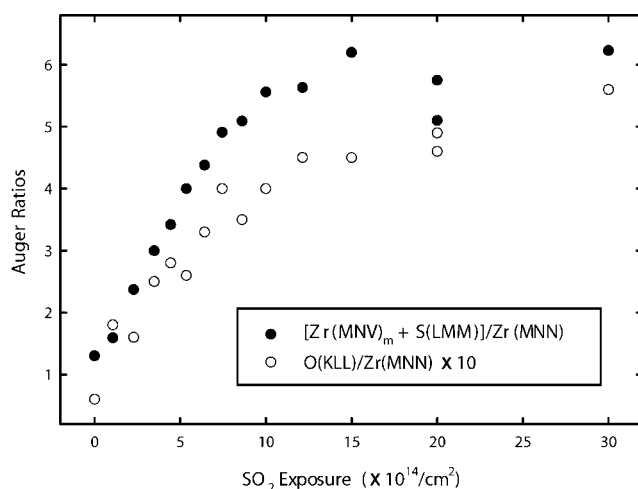


Figure 1. The $[\text{Zr}(\text{MNV})_m + \text{S}(\text{LMM})]/\text{Zr}(\text{MNN})$ and $\text{O}(\text{KLL})/\text{Zr}(\text{MNN})$ Auger ratios as a function of SO_2 exposure at 300 K. The calculated $\text{O}(\text{KLL})/\text{Zr}(\text{MNN})$ ratio is multiplied by 10. Note the apparent saturation in sulfur and oxygen Auger signatures near exposures of $10.0 \times 10^{14}/\text{cm}^2$.

Figure 2(A) shows zirconium and sulfur Auger electron spectra after $20.0 \times 10^{14}/\text{cm}^2$ exposure to SO_2 at 300 K, and after various subsequent exposures to H_2O at 150 K. Our motivation for subsequent H_2O adsorption at 150 K is primarily in investigating the effect of pre-adsorbed impurities on the high-temperature desorption of water, observed after low-temperature adsorption.² The uppermost spectral line in the figure is from a Zry-4 surface after SO_2 adsorption, prior to exposure to H_2O . Exposure to SO_2 ($20.0 \times 10^{14}/\text{cm}^2$) induces a shift in the $\text{Zr}(\text{MNN})$ feature by about 3.0 eV and appears to saturate the surface, as Fig. 1 indicates. The presence of sulfur is best reflected in the increased intensity of the overlapping $[\text{Zr}(\text{MNV})_m + \text{S}(\text{LMM})]$ Auger feature and its shift toward higher kinetic energies.¹⁰

Note that after water adsorption this overlapping feature decreases in intensity and undergoes significant line shape changes. Adsorbates either occupy sites above sulfur or push sulfur deeper into the subsurface or both. In any case, the reduction in the intensity of the overlapping feature primarily reflects how adsorbed water molecules attenuate sulfur electrons from the LMM transitions. Note that after water exposure of $50.0 \times 10^{14}/\text{cm}^2$ the intensity of the overlapping feature is drastically reduced and a low-energy shoulder of this feature starts to grow. This feature corresponds to oxidized zirconium, $\text{Zr}(\text{MNV})_o$.^{7,8} Even though the $\text{Zr}(\text{MNV})_m + \text{S}(\text{LMM})$ feature undergoes changes of intensity and shape up to water exposures of $350.0 \times 10^{14}/\text{cm}^2$ and the $\text{Zr}(\text{MNV})_o$ feature continues to grow, no changes in the position of the $\text{Zr}(\text{MNN})$ feature (0.3 eV uncertainty) are observed.

These results indicate that water adsorbed on top of sulfur does not further oxidize the surface to a higher oxidation state. Since in the process of water adsorption there is no further shift in the $\text{Zr}(\text{MNN})$ feature toward lower energies, adsorption of water on sulfur and oxygen covered Zry-4 only allows the $\text{Zr}(\text{MNV})_o$ feature to become more visible. It would be interesting to study this system with X-ray photoelectron spectroscopy or secondary ion mass spectrometry, but we presently cannot do such studies in combination with controlled gas exposures and linear temperature ramping.

Our recent study of 150 K H_2O adsorption on clean Zry-4 showed that the $\text{Zr}(\text{MNN})$ feature shifts by about 4.5 eV after higher exposures,² whereas in the present study the shift of 3.0 eV induced by SO_2 adsorption is not further shifted by subsequent H_2O adsorption. It is interesting that even though adsorbed water suppresses the AES signature of sulfur and results in the appearance of an oxidized zirconium feature, $\text{Zr}(\text{MNV})_o$, it does not affect the oxidation state of zirconium, as monitored through the $\text{Zr}(\text{MNN})$ transition. There are two plausible explanations for this. One possibility is that adsorbed water, most likely in the form of dissociated fragments,¹⁴ is not chemically active and only attenuates the sulfur Auger signal. Another possibility is that dissociated water fragments oxidize available metallic zirconium to the same oxidation state as induced by SO_2 adsorption, which manifests itself as an increase in the $\text{Zr}(\text{MNV})_o$ signal intensity. Whatever the case, since the adsorption of water on

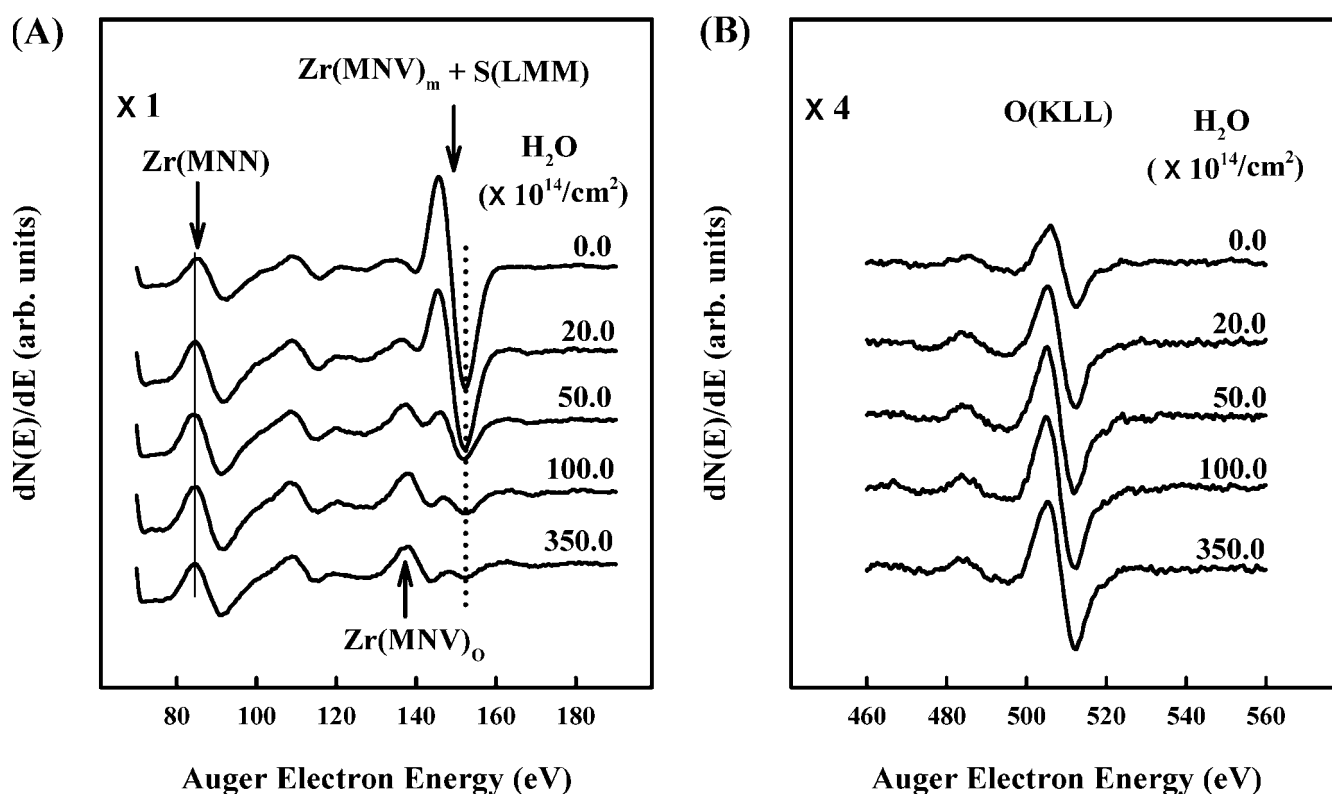


Figure 2. Auger electron spectra following adsorption of H₂O on SO₂/Zry-4. Exposure to SO₂ ($20.0 \times 10^{14}/\text{cm}^2$) was performed at 300 K followed by various exposures to H₂O at 150 K. Panel (A) reveals how zirconium and sulfur Auger features are affected, whereas panel (B) shows the behavior of the O(KLL) Auger signal. The intensity of the overlapping [Zr(MNV)_m + S(LMM)] Auger feature is reduced, whereas the oxidized zirconium feature, Zr(MNV)_o, develops with increasing H₂O exposure. The vertical scale of panel (B) is four times that of panel (A).

clean Zry-4 surface results in a larger shift of the Zr(MNN) transition, it seems that pre-exposed surface impurities (S and O) have an effect on the resulting surface oxidation state.

Note the dotted line on the negative feature inserted in Fig. 2(A). We would like to point out that even though it is common in the literature to insert a line to emphasize the downward shift⁷ of the Zr(MNV) transition, an emphasis of the upward shift² is probably a more precise way of detecting surface oxidation. For example, in a study of H₂O adsorption on zirconium at room temperature no shift in the Zr(MNV) transition was reported on the basis of the monitoring of the negative peak⁷, whereas visual inspection of the spectra indicates a shift in the positive peak position toward lower energies. Our water adsorption experiments reveal that the positive Zr(MNV) peak, not the negative one, undergoes significant changes during water adsorption.²

Figure 2(B) shows the same H₂O exposure sequence on SO₂ pre-exposed Zry-4 surfaces as Fig. 2(A), with a focus on the oxygen KLL Auger signal. The uppermost spectral line represents oxygen from dissociated SO₂. Note how water exposures of 20.0 and 50.0 $\times 10^{14}/\text{cm}^2$ result in an increase of the O(KLL) feature, whereas further H₂O exposures have very little effect on the peak-to-peak height. Higher exposures to H₂O of 100.0 and 350.0 $\times 10^{14}/\text{cm}^2$ do not change the oxygen Auger signal significantly but instead change the shape of the overlapping [Zr(MNV)_m + S(LMM)] Auger feature, making the oxide feature Zr(MNV)_o more dominant (Fig. 2(A)). We propose that even though the

near-surface region appears to saturate with oxygen, H₂O adsorption still takes place over a wide exposure range.

Figure 3 shows the effect of H₂O adsorption on SO₂ pre-exposed Zry-4 surfaces on the zirconium and sulfur Auger features, in terms of Auger ratios. Note that the [Zr(MNV)_m + S(LMM)]/Zr(MNN) and Zr(MNV)_o/Zr(MNN) data show opposite trends. It is interesting that the [Zr(MNV)_m + S(LMM)]/Zr(MNN) initially shows a rapid drop, whereas the Zr(MNV)_o/Zr(MNN) ratio does not show an initial rapid increase. This implies that detection of the oxide feature, Zr(MNV)_o, is suppressed by the intense S(LMM) feature at low H₂O exposures. Owing to the gettering nature of zirconium and the difficulty in keeping its surface clean, it is important to establish the role of impurities (sulfur and oxygen) on the desorption characteristics of water. From our AES results, it is evident that SO₂ adsorption prevents any subsequent shift in the Zr(MNN) feature that would indicate further changes in oxidation state of the already-oxidized zirconium.

Figure 4 presents TPD spectra of water following water adsorption on a clean Zry-4 surface (a), and on surfaces pre-exposed to 5.0 $\times 10^{14}$ SO₂/cm² (b) and 20.0 $\times 10^{14}$ SO₂/cm² (c). In all three cases, the same exposure to H₂O (150.0 $\times 10^{14}/\text{cm}^2$) was used. Water adsorption on clean Zry-4 surfaces (a) results in desorption with three overlapping features as reported previously.² Adsorption of H₂O on a Zry-4 surface partially covered with sulfur and oxygen exhibits a slightly different TPD profile and a greater amount

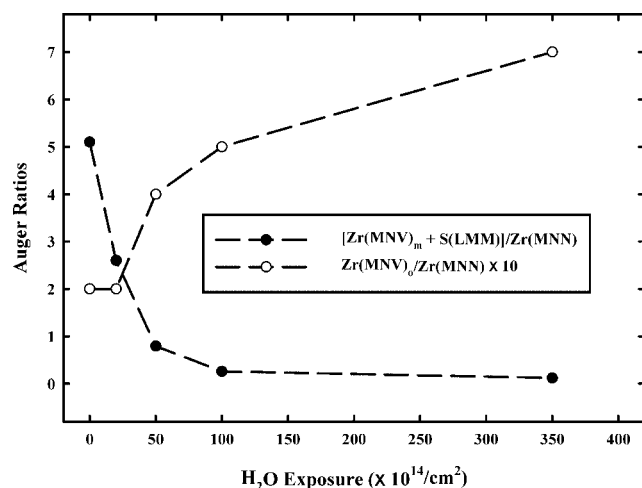


Figure 3. The $[\text{Zr}(\text{MNV})_m + \text{S}(\text{LMM})]/\text{Zr}(\text{MNN})$ and $\text{Zr}(\text{MNV})_o/\text{Zr}(\text{MNN})$ Auger ratios as a function of H_2O exposure on Zry-4 pre-exposed to $20.0 \times 10^{14} \text{ SO}_2/\text{cm}^2$.

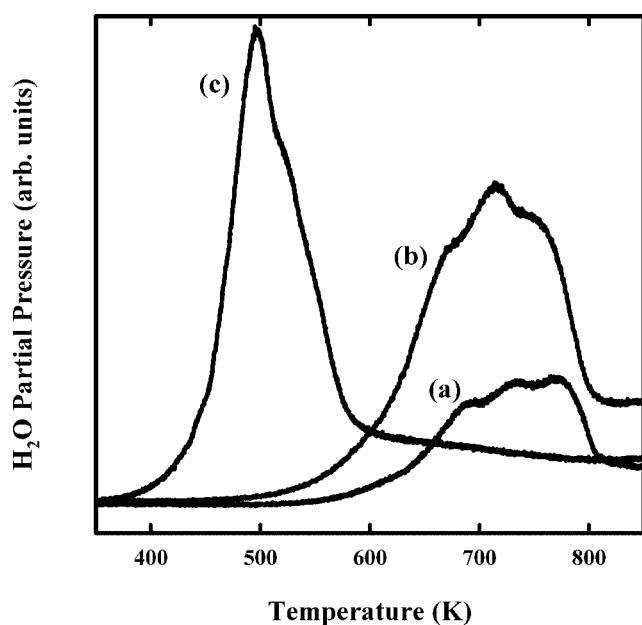


Figure 4. TPD spectra of water following water exposures of $150.0 \times 10^{14}/\text{cm}^2$ on three different surfaces. Adsorption on cleaned Zry-4 (a), a surface pre-exposed to $5.0 \times 10^{14} \text{ SO}_2/\text{cm}^2$ (b), and a surface pre-exposed to $20.0 \times 10^{14} \text{ SO}_2/\text{cm}^2$ (c). Exposure to sulfur dioxide was performed at 300 K followed by exposure to water at 150 K.

of molecular water desorption (b). This time the middle feature dominates. The fact that more water desorbs from SO_2 pre-exposed surfaces can be explained by the presence of impurities, particularly sulfur, that affect diffusion of oxygen into the bulk during heating to high temperatures. This diffusion competes with desorption.

Following H_2O adsorption on a clean surface (a), subsequent heating dissolves part of the oxygen, whereas some other parts participate in the formation and desorption of water.¹⁵ Adsorption of H_2O on Zry-4 surfaces pre-exposed to SO_2 ((b) and (c)) results in 2–3 times greater desorption yields. The large decrease in desorption peak temperature

also indicates the involvement of sulfur in preventing diffusion of oxygen into the subsurface region. Even though the temperature is drastically reduced by the presence of sulfur, the desorption of H_2O near 500 K from Zry-4 is unusually high when compared to desorption from other metal surfaces.^{16,17}

Both experimental^{18–20} and studies from the first-principles²¹ of oxygen adsorption on zirconium indicate population of subsurface sites at low coverages. Therefore, desorption of water above 700 K when no sulfur is present most likely involves subsurface species. This interpretation is consistent with an earlier study of 100 K water adsorption on polycrystalline Zr where mostly O_{ads} and H_{ads} were detected with small amounts of OH_{ads} .¹⁴ It is possible that a sulfur-contaminated surface prevents or affects the diffusion of these dissociation fragments into subsurface sites, which results in the desorption of water at much lower temperatures. Consistent with this, the desorption peak is narrower since surface processes dominate. The picture that we propose from our TPD results in which S stays beneath adsorbed water and blocks the population of subsurface sites is consistent with our AES results. We propose that sulfur-rich Zry-4 surfaces do not prevent water adsorption, and that water is probably not fully dissociated upon adsorption. The presence of sulfur near the surface affects the diffusion of hydrogen and oxygen into the bulk, which is reflected in different recombination mechanisms. In addition, the high affinity of Zr toward oxygen is probably reduced on the sulfur-saturated surface allowing oxygen to leave the surface in the form of water at much lower temperatures.

CONCLUSIONS

Dissociation of sulfur dioxide on Zry-4 at 300 K results in surface oxidation, as indicated by a shift of 3.0 eV of the $\text{Zr}(\text{MNN})$ Auger transition. Subsequent adsorption of water on sulfur- and oxygen-contaminated surfaces results in the appearance of a zirconium oxide Auger feature, $\text{Zr}(\text{MNV})_o$, but does not shift the $\text{Zr}(\text{MNN})$ feature further. There are two possible explanations for this. Adsorbed water dissociates on the surface and the oxide layer grows in thickness without further affecting the final oxidation state of zirconium, or adsorbates only attenuate the sulfur Auger signal making the $\text{Zr}(\text{MNV})_o$ feature more noticeable. We find that saturating the surface with sulfur and oxygen drastically affects water desorption kinetics. Desorption peak maxima are shifted 200 to 300 K toward lower temperatures with 2–3 times larger yields, primarily attributed to the presence of sulfur.

Acknowledgement

We thank Wah Chang for providing us with Zry-4 materials.

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