

The interaction of water vapor and hydrogen water mixtures with a polycrystalline uranium surface*

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The initial room-temperature interactions of water vapor with polycrystalline bulk annealed uranium surfaces were studied by combined measurements utilizing Direct Recoil Spectrometry (DRS) and X-ray Photoelectron Spectroscopy (XPS). It was found that the water goes through a complete dissociation into oxidic oxygen and two neutral H atoms throughout the whole exposure range. The process proceeds by two consecutive stages: (i) below about 80% monolayer coverage, the dissociation products chemisorb mainly on the remaining non-reacted metallic surface by a simple Langmuir-type process; (ii) Between about 80% and full coverage, three dimensional oxide islands (that start to form at 50–60% coverage) cover most of the surface and full dissociation continues on top of them, with part of the hydrogen staying on top of the oxide. It was also found that traces of about 2% water vapor are sufficient to inhibit hydrogen dissociation and chemisorption on uranium surfaces, under low pressure exposures, at room temperature. The efficiency of the inhibition increases with temperature in the range of 200 – 400 K. The inhibition effect is also influenced by the extent of residual strain of the sample, with increasing inhibition efficiencies exhibited by a less strained surface. O₂, in contrast to H₂O, is not an inhibitor to surface adsorption and dissociation of hydrogen. Three types of mechanisms are discussed in order to account for the above inhibition effect of water. It is concluded that the most probable mechanism involves the reversible adsorption of water molecules on hydrogen dissociation sites causing their “blocking”.

* Invited article

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1. INTRODUCTION

Understanding the interactions of hydrogen and water vapor with metallic surfaces is an important issue due to its relation to environmental corrosion processes. Yet, studies on the very initial steps of these interactions, especially at ambient temperatures, are not adequately completed. It is commonly accepted that most of the transition metals tend to dissociate adsorbed water at room temperature [1]. The dissociation may be complete (i.e. into $2\text{H}+\text{O}$), partial (i.e. into $\text{H}+\text{OH}$) or a combination of these two possibilities. Hence, a mixture of H, O and OH entities is generally anticipated to accumulate on metallic surfaces exposed to water. A common damage caused by hydrogen in metals is embrittlement, as well as hydride formation, by a heterogeneous attack of the surface by hydrogen gas.

Secondary ion mass spectroscopy (SIMS), XPS, Auger electron spectroscopy (AES), ultra-violet photoelectron spectroscopy (UPS) and Temperature program desorption (TPD), were applied before, to the study of the water-uranium reaction [2-4]. The reaction of water with UO_2 was also studied [5-8], using, besides the above techniques, also Electron stimulated desorption (ESD), low energy electron diffraction (LEED) and low energy ion scattering (LEIS). Winner *et al.* [2] proposed fast oxidation and strongly bound OH- species on the formed oxide. Balooch and Hamza [3], on one hand, attributed low temperature desorption of H_2 in the TPD measurements to hydrogen adsorbed on top of the formed oxide. Stultz *et al.* [7] and Senanayake and Idriss [8] also claimed the same about hydrogen adsorbed on defects on $\text{UO}_2(100)$ and $\text{UO}_2(111)$ surfaces respectively. Manner *et al.* [4], on the other hand, performed a careful study of H_2 desorption vs. surface coverage and claimed that hydrogen resides only on non oxygen (or oxide) covered patches of the uranium surface and H_2 desorption from a totally covered (non defective) surface stems from subsurface hydrogen.

It is well known that most conventional surface analysis techniques are either not capable of probing directly surface hydrogen, or (e.g. SIMS) have some limitations in interpreting H surface concentrations [9-12]. A complementary powerful technique for such studies is the direct recoils spectrometry (DRS) previously reviewed [10-12]. This method is insensitive to ion-fractions, hence to chemical matrix effects changes, which enables the decoupling between chemical and concentration parameters. Also, unlike SIMS or electron spectroscopy methods, DRS can probe different atomic geometrical arrangements on the surface due to its sensitivity to shadowing/blocking effects [10,12,14,15].

Exposing a UHV chamber to water vapor increases instantly hydrogen presence at the residual gas phase due to water dissociation on the interior surface of the vacuum chamber. In the study of reaction of H_2O with various

uranium surfaces [9], it was evident that there was no effect of background hydrogen in the vacuum chamber, for various $\text{H}_2\text{O}/\text{H}_2$ ratios (even for ratios <1). On the other hand, exposure of uranium to "clean" hydrogen (the actual amount of residual water vapor was not measured but estimated to be negligible) yielded clear, Langmuir like hydrogen chemisorption on the surface [13]. It is evident, therefore, that above a certain $\text{H}_2\text{O}/\text{H}_2$ ratio, the hydrogen has no effect on the water chemisorption kinetics, i.e. the presence of water totally prevents hydrogen chemisorption and only below a certain ratio hydrogen chemisorption occurs.

In this study, we present the results obtained for a strain-relieved (heated in the UHV system to 520 K for 48 hours) polycrystalline uranium sample. The initial strain was created during hot-worked rolling of the metallic uranium. Wider studies of water vapor dissociation, adsorption and initial oxidation [9], presented the strain effects on the adsorption and initial oxidation mechanisms of water products on uranium surfaces, as well as the effects of the strain on the inhibition of hydrogen adsorption by water vapor [16].

The goals of the study, summarized in this presentation, were: 1) to characterize and understand the mechanism of dissociation, adsorption of water vapor on the surface and the initial oxidation of uranium by it; 2) to determine the limiting $\text{H}_2\text{O}/\text{H}_2$ ratio of inhibition of hydrogen adsorption on the uranium surface; and 3) to understand the inhibition mechanism of the water on H_2 chemisorption. A model is given, differentiating between the possible routes of water dissociation, adsorption and reaction on the surface and the specific $\text{H}_2\text{O}/\text{U}$ is analyzed accordingly. The $\text{H}_2/\text{H}_2\text{O}$ ratio for the inhibition of H_2 adsorption is presented and three possible mechanisms for the inhibition effect of water are discussed, of which one mechanism seems to be valid in the present case. A comparative measurement where oxygen replaces water vapor is also presented and conclusions are drawn as to the role of the water dissociation products on the inhibition mechanism.

2. EXPERIMENTAL

An ultra-high-vacuum (UHV) chamber ($\sim 2 \times 10^{-10}$ Torr baseline pressure) incorporated with DRS [10-12], that monitors relative concentrations of surface hydrogen and oxygen, was used in the present study. The DRS technique (Fig. 1), is extremely surface sensitive, probing the topmost atomic layer of the solid, being sensitive to surface concentrations of the solid, being sensitive to surface concentrations of about an order of magnitude lower than AES or XPS. Due to the grazing angle used, geometrical information may be gained from the effects of shadowing of hydrogen atoms by neighboring larger atoms [10,12,14] (see discussion). The technique is essentially non destructive, due to the low primary ion dose required to acquire a typical spectrum ($\sim 10^{11}$ ions/cm²). We

have used 3 Kev Ar^+ ions. The electron multiplier detector is equally sensitive to the impact of energetic (hundreds of eV) ions and neutrals, hence the insensitivity to the charge state of the recoils.

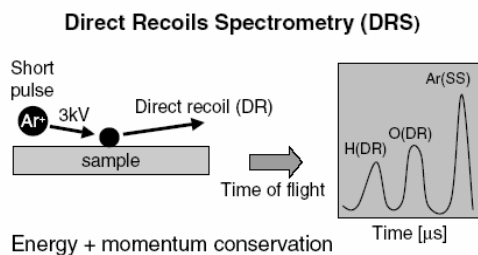


Fig. 1. A schematic representation of the direct recoil (DR) process and products. SS – single scattering.

The sample was mechanically polished down to $1\mu\text{m}$ smoothness, using diamond paste, leading to a mirror like surface, cleaned in distilled water, acetone and ethanol. It was heated to $\sim 520\text{ K}$ for ~ 48 hours. Sputter cleaning was performed by a rastered, differentially pumped ion gun, using 5 keV Ar^+ ions, with a current of about $5\ \mu\text{A}/\text{cm}^2$. Sputtering was carried long enough; so that the oxidized surface layer as well as the polishing work hardened one, were removed. Distilled water, contained in a stainless steel reactor, was used after a few freeze-pump-thaw cycles in order to reduce the gases dissolved in the water.

Water vapor, hydrogen and oxygen pressure in the chamber were controlled by leak valves. The water cleanliness, hydrogen, water vapor and oxygen pressures, during exposure, were monitored by residual gas analysis (RGA). DRS measurements were performed with continuous exposures during the measurement. All exposures were performed by backfilling the UHV chamber with gas, measuring the pressure with a Bayard-Alpert gauge and regulating the H_2O or H_2 partial pressure with the RGA. The ratios between the different gases are molar (measured by their relative pressures). Exposures and measurements, presented in the present study, were performed isothermally at room temperature (RT), 200 K and 400 K.

3. RESULTS

3.1. H_2O

Fig. 2a presents O(DR) and H(DR) exposure lines and Fig. 2b depicts the $\text{H(DR)}/\text{O(DR)}$ ratio vs. the exposure dose (expressed in Langmuirs, $1\text{L} = 10^{-6}\text{ Torr}\times\text{sec}$) for three water exposure pressures. The O(DR) intensity was normalized so that the saturation value attains unity (being sensitive to the

outermost monolayer). Unlike the monotonous behavior displayed by the O(DR) curve, reaching a saturation (i.e. dose independent) value at ~ 10 L, the exposure behavior of the H(DR) intensities is rather complex. It initially increases with increasing exposure dose, reaching a maximum value at a very low exposure (1-2.5 L, pressure dependent), then decreasing with further exposure, attaining a minimum at about 4-5 L, then the intensity increases reaching finally a saturation value at about 13 L.

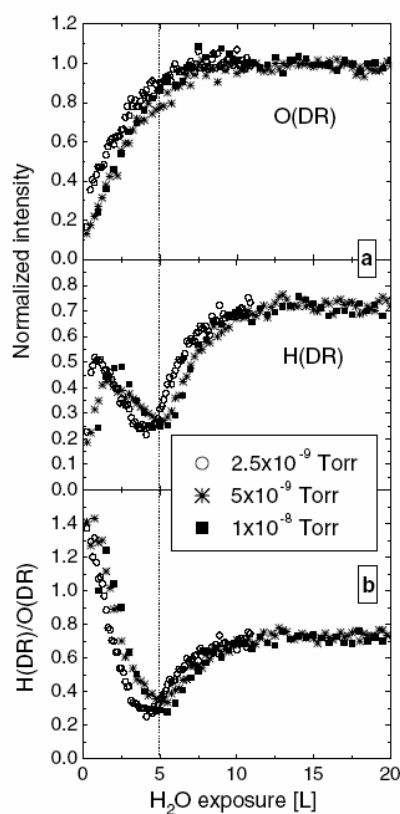


Fig. 2. a) O(DR) and H(DR) vs. H₂O exposure, for 3 exposure pressures. The saturation value of O(DR) is normalized to 1 (full coverage). The minimum of H(DR) is marked by a dashed line; b) H(DR)/O(DR) vs. H₂O exposure.

Some indication on the chemical nature of the water-uranium reaction products can be obtained from the XPS measurements of the oxygen O 1s and uranium U 4f core level peaks, given in Figs. 3&4. Fig. 3 displays XPS measurements of the O 1s line for the 2,5 and 20 L H₂O exposures (at 2×10^{-9} Torr) together with that of 30 L O₂/U and 20 L H₂O at 200 K (for comparison). It

is clear that for all the ambient temperature exposures only oxidic oxygen is observed, compared to the low temperature exposure, where a strong contribution shifted about 1.5 eV to a higher binding energy (HBE), typical to hydroxylic oxygen, is observed (even though some other oxygen-related species can account for some HBE peaks [2]). It should be pointed out that according to the DRS curves (Fig. 2), which are discussed later, hydrogen is continuously accumulating on the surface and is significantly present at these higher exposures. This hydrogen, however, does not seem to be associated with hydroxyls, as indicated by the above XPS results. Fig. 4 presents the corresponding U 4f core level peaks (together with these for clean uranium), that provide a quite sensitive probe for the oxidation state of the near-surface uranium atoms [2]. Even for 2 L it is clear that the surface is slightly oxidized (formation of U^{+4} ions), and for 20 L the oxide peak is predominating. Hence, the higher H_2O exposure range is associated with oxide formation and accumulated H atoms on top of it, as indicated by DRS.

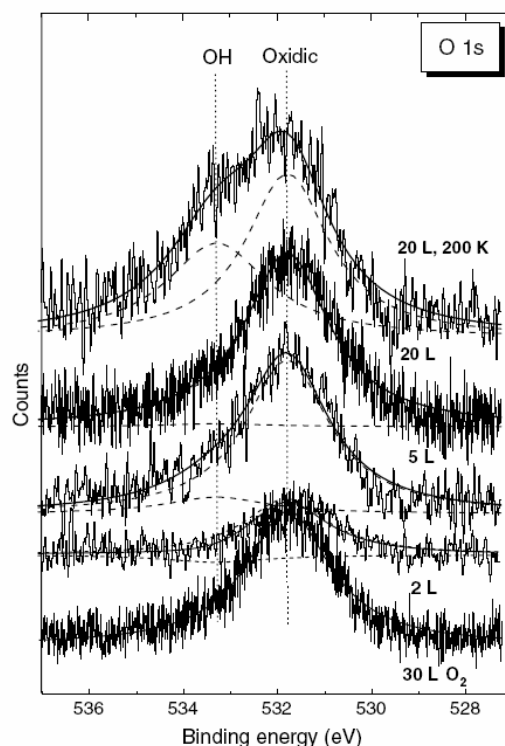


Fig. 3. XPS O 1s line for 5, 10 and 40 L water vapor exposure at ambient temperature (AT), together with that of 40 L taken at 200 K and 50 L O_2 AT exposure. Lorentzian fits for oxidic and OH contributions are plotted. The parameters of the oxidic contribution were fixed in the water exposure fits to those obtained for the O_2 one.

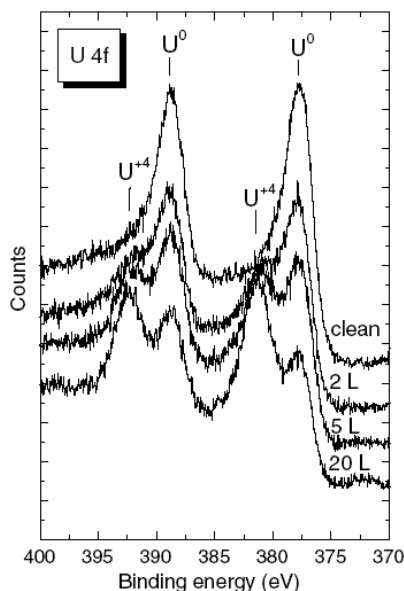


Fig. 4. XPS U 4f lines for clean uranium and 5, 10 and 40 L water vapor exposures. The energy of metallic and (+4) uranium are indicated.

These H's are most likely attached to surface oxidic oxygen atoms, however they do not form conventional hydroxyl groups, as indicated by the absence of a shifted O 1s XPS peak. The H atoms on the polycrystalline surface may be multiply influenced by adjacent surface oxygen atoms and complex surface coordination may be the cause for the lack of O1s core level shift in the XPS spectrum. These results resemble those of Winer *et al* [2], that under similar exposures (of D₂O), obtained a surface product that probably contained OD groups (as probed by SIMS), but did not display typical XPS hydroxylic peaks. This issue will be further discussed in Sec. 4.

3.2. H₂+H₂O mixtures

For water vapor to hydrogen ratios (H₂O/H₂, henceforth denoted as W/H) above 1/100, the measured ratio of directly-recoiled hydrogen to directly-recoiled oxygen H(DR)/O(DR), (henceforth denoted H/O) is the choice of presentation, since presenting H(DR) is ambiguous due to contributions from H₂ as well as from H₂O. For W/H=1/500 or lower water vapor concentrations, the contribution of both H(DR) and O(DR) from water vapor dissociation is negligible and therefore H(DR) is presented. Fig. 5 depicts H/O vs. the exposure dose of both water (Fig. 5a) and H₂ (Fig. 5b) for mixtures with different W/H values. Fig. 6 depicts H(DR) vs. H₂ exposure for W/H=1/500 and for lower

water vapor concentrations ($W/H = 1/2,000, 1/50,000$). It is seen that for W/H ratios of 10, $1/3$ and $1/50$ the obtained exposure curves behave exactly the same as that of pure water (Fig. 2), i.e. no additional accumulation of H is obtained even for much higher exposures to H_2 in these mixture. Only for W/H ratios that decrease to about $1/100$ or lower a different behavior, with additional H chemisorption due to H_2 , is obtained. For the very low W/H ratios presented in Fig. 6, the adsorption curves are identical for all ratios presented, and behave as for pure H_2 [13].

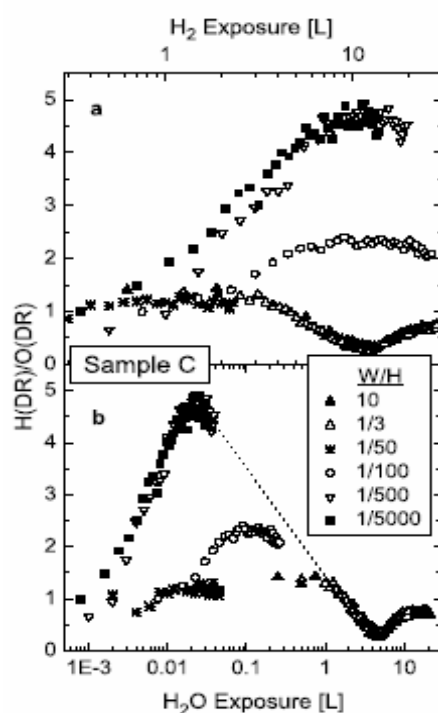


Fig. 5. Exposure curves, performed at room temperature, for different W/H mixture ratios, with a fixed partial pressure of H_2 (2×10^{-8} Torr). (a) H/O versus H_2 exposure dose. (b) H/O versus the corresponding H_2O exposure dose.

It is evident, thus, that the presence of relatively low concentrations of water ($\sim 2\%$) in the H_2O+H_2 mixtures inhibits the H_2 chemisorption on the uranium surface. For very low concentration of H_2O when no inhibition occurs (below the inhibition limits stated above, i.e. below about 2% H_2O in the mixture), an initial additional accumulation of H is observed due to H_2 chemisorption. However, even for these cases when the H_2O exposure dose (in a given mixture) exceeds a certain limit, it is seen that a decrease in the H/O ratio starts to take place

probably due to the replacement of the initially chemisorbed excess H by the O dissociation fragments of the water.

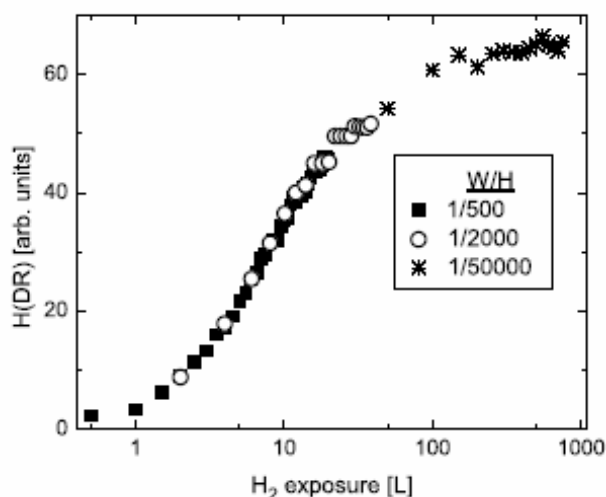


Fig. 6. H(DR) vs. H₂ exposure dose, for different W/H mixture ratios and low water vapor concentrations.

The temperature effect on the inhibition efficiency is illustrated in Fig. 7. It is seen that the inhibition ability of water is increased with increasing temperature (i.e. no H₂ chemisorption at 400 K compared to a rapid chemisorption at 200 K, for the same constant H₂O+H₂ mixture, W/H=1/100). In the range of 200-400 K, hydrogen adsorption, if not inhibited, is not dependent much on temperature. Above 400 K, desorption occurs. Heating up to 400 K did not change the initial sticking coefficient, S₀, calculated according to the clustering model, which yielded 0.2 for hydrogen accumulation due to H₂ chemisorption.

As for the effect of oxygen, Fig. 8 presents O(DR) and H(DR) exposure curves (normalized to the saturation value of the pure gases) for the mixture O₂/H₂ = 1/10, together with the adsorption curves of pure H₂ and O₂ (the dose of the latter is presented by the upper abscissa). It is seen that unlike H₂O, oxygen does not display an inhibition effect on H₂ chemisorption, and the initial accumulation rates of H are the same with the O₂+H₂ mixture as with pure H₂. However, oxygen replaces hydrogen (or shadows H sites) as the chemisorption proceeds. Fig. 9 presents D₂ adsorption curves on the clean metallic surface and also following pre-exposures to two doses of water.

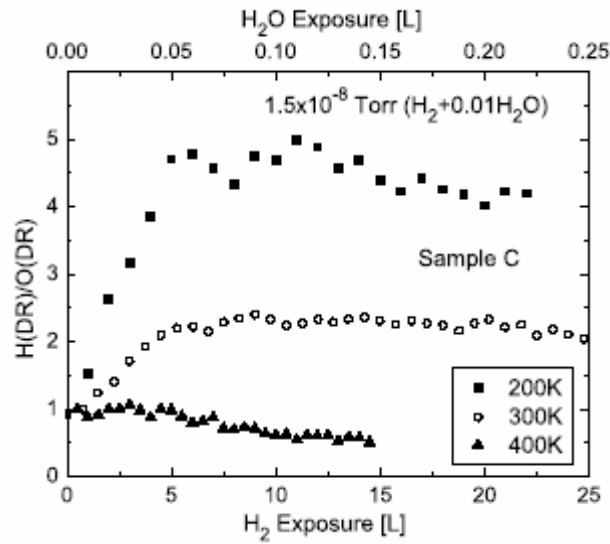


Fig. 7. H/O vs. H_2 exposure at various temperatures, for $W/H = 1/100$.

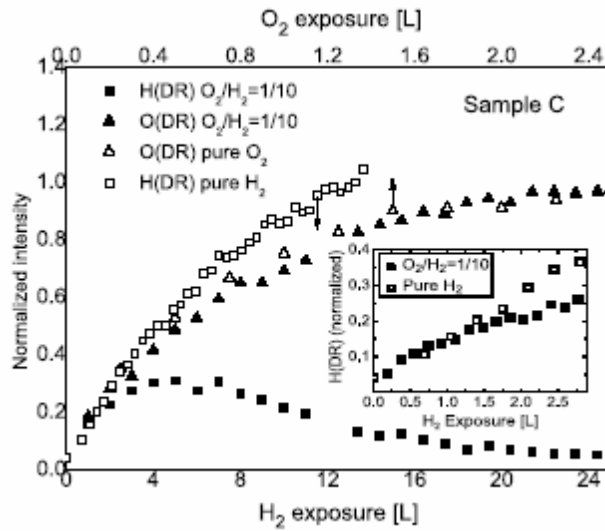


Fig. 8. H(DR) and O(DR) vs. H_2 and O_2 exposure dose, for a given H_2+O_2 mixture $O_2/H_2 = 1/10$ and for the pure gases. Inset: H(DR) vs. H_2 and H_2+O_2 exposures for the low exposure range.

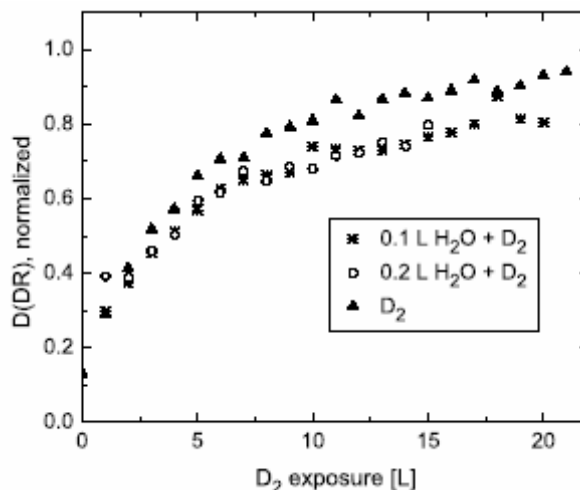


Fig. 9. The intensity variations of the D(DR) signal versus D₂ exposure for different preexposures to H₂O (0,0.1,0.2 L) at room temperature.

4. DISCUSSION

4.1. The shadowing model

The shadowing model was presented in previous publications [14,15]. Essentially, it makes use of shadowing of surface H's by neighboring oxygen atoms, while H's sitting on top of O's (OH) are not shadowed. This enables the distinction between partial ($\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$) and full dissociation ($\text{H}_2\text{O} \rightarrow \text{O} + 2\text{H}$). Fig. 10 is a schematic representation of the two routes possible for the direct-collision (Langmuir-type) chemisorption mechanism of water on a metallic surface. Partial dissociation yields an attenuation factor of 2 between the initial coverage H(DR)/O(DR) ratio to the final one. For full dissociation, the attenuation factor is infinity. An attenuation factor between 2 and infinity, points to a mixture of the full and partial dissociation routes.

4.3. Oxygen and hydrogen accumulation for H₂O exposures

O(DR) indicates the surface coverage with oxygen, that can be in the form of adsorbed oxygen or OH and in a certain stage transform into an oxide. H(DR)/O(DR) together with the O 1s XPS spectrum (Fig. 3) determines the surface state of adsorbed oxygen, while the U 4f spectrum (Fig. 4) depicts the appearance of the U⁺⁴ peak, associated with oxide formation (UO₂). O(DR) was successfully fitted to the clustering model [18] rather than to the double site one (not shown). The DRS curve (Fig. 2), indicates hydrogen continuous accumulation on the surface.

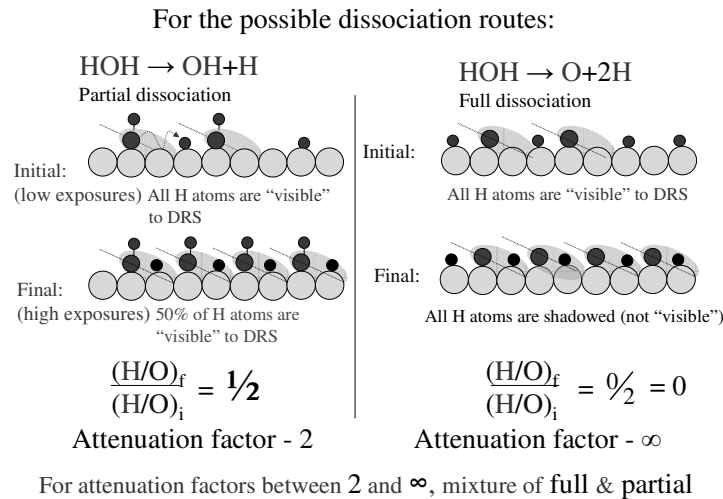


Fig. 10. A schematic representation of the two routes possible for the direct-collision (Langmuir-type) chemisorption mechanism on a metallic surface.

4.3. Inhibition of hydrogen chemisorption on uranium surfaces by traces of water vapor

As mentioned in Section 3, Figs. 5–7 illustrate the inhibition effect of water on the H_2 chemisorption process. For the pure water adsorption [9,14,15], the hydrogen atoms, originating from the full dissociation of water on the metallic surface can be shadowed by neighboring oxygen atoms, an effect that increases with increasing exposure, accounting for the minimum, observed in the $\text{H}(\text{DR})/\text{O}(\text{DR})$ ratio [14,15]. At a more progressive stage, when an oxide layer is formed, only partial dissociation of water occurs, with non shadowed OH groups, located on top of the oxide, which accounts for the increase of the $\text{H}(\text{DR})/\text{O}(\text{DR})$ ratio, for this stage. It is seen that down to a W/H ratio of about 1/50 the chemisorption behavior of the $\text{H}_2 + \text{H}_2\text{O}$ mixture behaves exactly as for pure water, i.e. in spite of the significant excess of H_2 in the mixture, no chemisorption of the H_2 takes place (which would change the displayed chemisorption curves) and only the accumulation of the H dissociation fragment of the water is dominating (as described in ref. [15]). Only at smaller W/H ratios of 1/100 and below the "signature" of H_2 starts to affect the exposure curves, attaining a pure H_2 like behavior at ratios below about 1/500 (Fig. 6).

One possible mechanism of the inhibition effect of water on the co-adsorption of H_2 may involve the capture of H_2 dissociation sites by the water dissociation fragments. The most likely fragment involved in such a process is H, due to his high mobility. Hence, according to this mechanism, the water-dissociated H

fragment that easily diffuses on the surface, strongly binds to the sites that also form H_2 dissociation sites, thus blocking further H_2 chemisorption. This mechanism may also be substantiated by the temperature trend observed (Fig. 7), indicating a more efficient inhibition ability of the water with increasing temperature. Such a trend may be accounted for by the increased diffusivity of H, leading to an enhanced capture of the H_2 dissociation sites by this fragment. Even though the above proposed mechanism is consistent with most experimental observations there is still one question related to its validity: If the H_2 dissociation sites are also preferred as binding sites to H, then a similar “blocking” of these sites should occur for pure H_2 (which also dissociates into $2H$), leading to the cessation of the H_2 chemisorption process even for pure H_2 (or for very low concentrations of water in the H_2+H_2O mixtures). A possible argument to settle the above question may be related to a difference in the chemical nature of the H originating from H_2O dissociation and that resulting from the H_2 dissociation (e.g. a different extent of ionicity, etc.). Such a difference may lead to different binding energies of the two H species to the H_2 dissociation sites, making the H fragment of water to bind strongly and irreversibly, whereas the H produced by H_2 dissociation to be bound more weakly not causing a “blocking” effect.

Another possible approach is to propose some alternative mechanisms that explain the different behavior of water and of pure H_2 , assuming both molecules yield the same H moiety by dissociation. Such possible mechanisms may involve a direct competition of the two molecules (H_2O and H_2) on the same adsorption sites, with a preference to the water molecules.

Two such mechanisms may be considered: first, assuming that the H_2 dissociation sites are also the energetically preferred dissociation sites of the water molecules. In this case, the H^0 dissociation fragment of the water (formed by an electron transfer from the U^0) may not be captured at the particular dissociation site but rather diffuse away across the surface. However, the O^{-2} fragment is bonded to the U^{+n} cation (n – the number of electrons transferred to the H^+ 's, i.e. $n = 2$ or 1 depending whether dissociation is full into $O^{-2} + 2H^0$ or partial into $OH + H^0$, respectively). Hence, the particular site is oxidized during water dissociation, and does not act anymore as an H_2 dissociation site. A second possibility is that the H_2 dissociation sites are also energetically preferred for H_2O adsorption (as a molecule), however, dissociation does not take place on these sites but requires the movement of the adsorbed H_2O molecule to a different set of sites. In this case the adsorbed H_2O molecules may still block the H_2 dissociation, yet, unlike the former possibility (oxidation of the sites) which induces an irreversible “poisoning” of the sites, this possibility is likely to induce a reversible effect, i.e. desorption of the adsorbed H_2O molecules under vacuum, may restore the H_2 dissociation ability.

It is thus possible to check the proper mechanism, by measuring the “memory effect” of water pre-exposure, on a subsequent H₂ exposure. It is anticipated that while H₂O dissociation–oxidation mechanism will display such “memory” of water pre-exposure, due to the irreversible oxidation of the sites, a molecular adsorption mechanism should not have such an irreversible effect, and a normal H₂ chemisorption should occur, following water exposure and pumping. Fig. 9 demonstrates the results of such measurements, where H₂O pre-exposures (pure H₂O, under a pressure equal to the H₂O partial pressure of the 1/50 mixture) were applied, followed by pumping and a subsequent D₂ exposure. (Deuterium was used in order to distinguish between the D₂ gas effect and the H accumulation due to water dissociation). It is evident that no “memory effect” is displayed, and the kinetics of D₂ chemisorption is almost not affected by the H₂O preexposure stage.

It is thus likely that the relevant inhibition mechanism in this case is the preferred molecular adsorption of the H₂O on the H₂ dissociation sites. As mentioned before, the inhibition efficiency is increasing with increasing temperature (Fig. 7). This trend can be accounted for by the reported temperature effect on the H₂O chemisorption mechanism [16]. It has been observed that at the lower temperature regime, the mechanism of water chemisorption involves a physisorbed precursor state, whereas the higher temperature mechanism is associated with a direct (Langmuir type) adsorption. It is thus anticipated that at the lower temperature regime most of the H₂ dissociation sites are not occupied by adsorbed H₂O molecules (which occupy the precursor state), thus no inhibition of H₂ chemisorption is induced. As the temperature increases, adsorption of the H₂O on the H₂ dissociation sites takes place, and inhibition starts to be effective.

As mentioned in the introduction a study was conducted on water adsorption [9] and hydrogen inhibition [17] on a series of samples, with successive steps of strain relief.

It was found that oxide growth for the more strained samples is mostly inwards, probably due to defects. For the more relaxed samples, the oxide grows mostly laterally. The sticking coefficient for oxygen, indicating the reactivity of the sample, decreases the more annealing is applied. This correlates well with the reduction of the number of bulk defects (that are manifested on the surface). Even though water has a deleterious effect on the chemisorption of H₂ for differently strained samples [17], a quantitative difference exists, with a more effective inhibition displayed by annealed samples, which require a smaller minimum concentration of H₂O to maintain inhibition. This trend is consistent with the increasing number of stress-induced defects present for the more stressed sample.

It is likely that stress-induced defects provide the H₂ dissociation sites, thus for the more stressed samples, a larger concentration of H₂O is required to induce effective inhibition (i.e. higher W/H limiting ratios). Such a view is substantiated by the higher reactivity of the stressed sample towards pure H₂ chemisorption [17].

5. SUMMARY AND CONCLUSIONS

1. DRS and XPS measurements point to a full dissociation of the H₂O molecules on top of the metallic surface as well as on top of the oxidic one. Electron transfer from the metal, in the initial stage, neutralizes the water H⁺s, that remain as chemisorbed neutral species on the metal surface. The anion oxygens form oxide islands that spread over the surface.
2. At about 80-90% coverage, the process continues by electron tunneling through the thin oxide to neutralize the water protons on the oxide. This reduction takes place probably by a two step mechanism, first producing OH⁻+H⁰ on the topmost oxidized surface and then reduction of the OH⁻ into O²⁻+H⁰ at the oxide-metal interface.
3. Traces of water vapor (ca. 1-2%) are sufficient to inhibit hydrogen gas chemisorption under low pressures, on metallic uranium surfaces.
4. The inhibition effect of water is temperature dependent, with increasing inhibition efficiencies obtained with increasing temperatures.
5. In contrast to H₂O, no inhibition of H₂ chemisorption is obtained by O₂ (in H₂+O₂ mixtures), within the corresponding O₂/H₂ ratios. Pre-exposure to water, prior to H₂ dosing, does not induce a "poisoning" effect. The inhibition effect of water is obtained only for H₂+H₂O mixtures (with a minimal H₂O concentration, i.e. 1-2%).
6. The most likely mechanism for the above effect is the reversible adsorption of H₂O molecules on H₂ dissociation sites; such adsorption seems to precede the irreversible dissociation of the water molecules. It takes place at higher temperatures (at about ambient and above), whereas at lower temperatures a different precursor state is preceding the H₂O dissociation step.

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