

Heat treatment effects on the surface chemisorption behavior of strained uranium: The H₂O/U reaction

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Abstract

The initial interaction of H₂O vapor with polycrystalline uranium surfaces was studied with samples initially strained, then strain relieved by heat treatments, performed in the temperature range up to ~650 K. The chemisorption characteristics of these surfaces were studied by a combination of direct recoils spectrometry and X-ray photoelectron spectroscopy. X-ray diffraction measurements were used to determine the level of strain relief induced by each of the heat treatments. For all the samples, full water dissociation on the metal surface is observed. The reactivity of the samples towards water is clearly strain dependent, with the sticking coefficient decreasing as strain is relieved. It also seems that for strained samples the initial growth of the oxide is mostly inwards, while for the more relaxed samples lateral growth is dominant. Two interesting phenomena were observed for specific samples. For the 420 K relieved sample, partial dissociation process is observed on top of the forming oxide, in contrast to the full dissociation observed for the other samples. For the ~650 K relieved sample, clustering of the adsorbed hydrogen atoms (resulted by water dissociation) on the metal surface is observed, in contrast to the homogeneous dispersion of H, occurring on the surface of all other samples. These two phenomena will further be studied in conjunction with microscopic metallurgical observations.

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1. Introduction

Understanding the interactions of water vapor and 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 to the extent that the complex mechanisms, controlling these reactions, are conclusively elucidated [1,2]. It is commonly accepted that most of the transition metals tend to dissociate the chemisorbed water at room temperature [1]. The dissociation may be complete (i.e. into 2H + O), partial (i.e. into H + 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. However, very few direct observations of these species and their kinetic behavior have been reported. One of the difficulties encountered in the studies of the interaction of water with metallic sur-

faces is the direct detection of hydrogen or hydrogen containing species, such as hydroxyl groups. For the latter, indirect probing such as chemical shifts in the accompanying O(1s) X-ray photoelectron spectroscopy (XPS) peaks [1], photon-stimulated desorption (PSD) or electron-stimulated desorption (ESD) [3,4] are sometimes used. However, such determinations are not conclusive and may be interpreted in different ways [1,2]. Other techniques, which in principle are sensitive to the presence of hydrogen atoms on the surface, utilized in some of these studies are secondary ion mass spectrometry (SIMS) and temperature programmed desorption (TPD). Still, as pointed out before [5,6], hydrogen signal intensities measured by most SIMS set-ups are strongly affected by the respective ion yield fractions, which turn to be sensitive to the chemical matrix effects. Hence the interpretation of such signal intensity variations is complicated by the convolution of two simultaneous factors, namely, surface concentrations and the above mentioned chemical matrix effects. The interpretation of TPD results is also somewhat ambiguous due to recombination effects (especially for hydrogen) on the surface and the inability, sometimes to distinguish between surface and subsurface products.

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A complementary powerful technique for such studies is the direct recoils spectrometry (DRS) previously reviewed [6,7]. 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 [5,6]). This capability can be used to elucidate geometry related phenomena associated with the surface chemisorption process. Thus, for example, it has been utilized in the study of the $\text{H}_2\text{O}/\text{Ti}$ system [2] to resolve between two parallel chemisorption routes—a direct-collision (Langmuir type) that yields isolated, perpendicular to the surface OH species, and a precursor state route yielding clusters of tilted OH moieties.

For the system $\text{H}_2\text{O}/\text{U}$, two studies, using the combination of DRS and electron spectroscopy, were lately performed by our group. The first study [8], was performed on a strained sample, slightly relieved (hence labeled Sample B) and the second one [9] on a more strain relieved sample (hence Sample C), revealing different mechanisms of adsorptions. In addition, SIMS, XPS, Auger electron spectroscopy (AES), ultra-violet photoelectron spectroscopy (UPS) and TPD were applied before, to the study of the water–uranium reaction [10–12]. The reaction of water with UO_2 was also studied [13–16], using, besides the above techniques, also ESD, low energy electron diffraction (LEED) and low energy ion scattering (LEIS). Winer et al. [10] proposed fast oxidation and strongly bound OH^- species on the formed oxide. Balooch and Hamza [11], 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. [15] and Senanayake and Idriss [16] also claimed the same about hydrogen adsorbed on defects on $\text{UO}_2(100)$ and $\text{UO}_2(111)$ surfaces respectively. Manner et al. [12], on the other hand, performed a careful study of H_2 desorption versus 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 known that the recrystallization process in uranium starts at approximately 600–700 K [17], while lower temperature annealing results in only recovery [17], meaning that the number of the dislocations are not reduced nor their density. Nevertheless, a rearrangement of the dislocations decreases the stress. Heating to higher temperatures and cooling causes grain growth and inflicts thermal strain due to the anisotropy of thermal expansion of uranium [18,19].

The present study concentrates on the effect of strain and its thermal relief on the surface processes and mechanisms. The main goal of the study was to try to correlate the surface processes to the bulk defects (dislocations) resulting from strain, inflicted on the samples and their cure by annealing. The current article summarizes the previous results published on this system [8,9], adds a large amount of new observations and presents an up-to-date whole picture the surface processes of the various heat treated samples and their correlations to the strain relief.

2. Experimental

2.1. The experimental system

An ultra-high-vacuum (UHV) chamber ($\sim 2 \times 10^{-10}$ Torr baseline pressure) incorporated with XPS and DRS [5–7], was used in the present study. The DRS technique is extremely surface-sensitive, probing the topmost atomic layer of the solid. Hence, combined measurements with electron spectroscopy methods (e.g. AES, XPS, etc.) may resolve between processes taking place on the outermost surface layer and those occurring at the subsurface region [20,21]. Due to the grazing angle used, geometrical information may be gained from the effects of shadowing of hydrogen atoms by neighboring larger ones.

2.2. Experimental procedures

Polycrystalline samples of strained (formed by hot worked rolling) uranium, treated thermally to partially or fully relieve the strain, were used in this study.

The samples were mechanically polished down to 1 μm smoothness, using diamond paste, leading to a mirror like surface, cleaned in distilled water, acetone and ethanol. One sample was studied as received (AR), and the others were heated, in the UHV system, to 420 K, 520 K or ~ 650 K for 48 h to relieve the strain. The samples will be named henceforth A for the not treated sample, and B, C and D, for the 420 K, 520 K and ~ 650 K treated samples, respectively.

The samples were scanned using an optical microscope and SEM (showing grains of ten micrometers size, not presented). XRD was performed on all of them.

In the UHV system, 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 the former stressed bulk will be reached. Distilled water contained in a stainless steel reactor was used after a few freeze–pump–thaw cycles in order to reduce the gases dissolves in the water, and the water (or oxygen) pressure in the chamber was controlled by a leak valve. The water cleanliness during exposure was monitored by residual gas analysis. The DRS measurements were performed with continuous exposure to water vapor during the measurement, while the XPS runs were performed following fixed doses of exposure. All exposures were performed by backfilling the UHV chamber with gas, measuring the pressure with a Bayard–Alpert gauge and regulating the H_2O stability with a mass-spectrometer.

All exposures and measurements, presented in the present study, were performed at room temperature (RT).

3. Results

XRD measurements performed on all the samples yielded different preferred orientations and line widths. For the [002] line, the widths are A: 0.35° , B: 0.23° , C and D: 0.17° .

Fig. 1A–D presents O(DR) and H(DR) exposure curves and Fig. 2 depicts the H(DR)/O(DR) ratio versus the exposure dose (expressed in Langmuirs, $1 \text{ L} = 10^{-6} \text{ Torr} \times \text{s}$) for all samples. In all graphs the O(DR) intensity was normalized so that the saturation value attains unity, while that of H(DR) scales to the normalized O(DR). For all samples except D (~ 650 K treatment), the H(DR) initially increases with increasing exposure dose, reaching a local maximum value at a very low exposure, then decreasing with further exposure, attaining a minimum followed by an intensity increases reaching finally a saturation value.

The chemical nature of the water–uranium reaction products can be partially obtained from the XPS measurements. Two regions of the spectrum are of interest in this study: the O 1s core level of the oxygen and the U 4f core level of the uranium peaks. Figs. 3 and 4 display the O 1s and U 4f, respectively, XPS measurements for Sample B for various exposures. In addition

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