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Amorphous carbon enhancement of hydrogen penetration into UO_2

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ABSTRACT

The interaction of D_2 and H_2O (humidity) with amorphous carbon covered UO_2 vs. clean UO_2 was studied using Secondary Ion Mass Spectrometry (SIMS) and X-ray Photoelectron Spectroscopy (XPS). It was found that SIMS depth profiles of the carbon covered side vs. the bare oxide, show significant higher intensities of H- and D- for the first, through the carbon layer and beneath it. The presence of a thin carbon layer on a UO_2 surface caused a significant buildup of hydroxyl, probably adsorbed on the carbon, but maybe also beneath the layer, in the presence of atmospheric humidity. Exposure of the carbon covered oxide to D_2 on a UHV annealed surface also caused a growth of the hydroxyl. It is concluded that the carbon surface strongly enhances the dissociation of water vapor as well as that of hydrogen and the penetration of the dissociation products to the oxide, as compared to the bare UO_2 surface. The contribution of the latter, beneath the carbon, should be verified or ruled out by further experiments.

Introduction

Uranium Dioxide (UO_2) is used mainly as fuel for nuclear reactors and in the manufacturing of radioisotopes. In some old reactors, uranium metal serves as nuclear fuel. The corrosion and hydrogen attack of uranium and uranium alloys are of great practical interest.

During storage of uranium rods in sealed containers, hydrogen pressure may evolve due to the reaction of the uranium with residual water [1,2]. An attack of the uranium may follow and cause hazardous hydride formation and brittleness [3,4]. For nuclear waste disposal, the enhanced oxidation and hydrogen formation can lead to a pressure buildup, and eventually a threat of breaching the storage container and a release of radioactive materials. Therefore, the safe disposal of uranium and UO_2 spent fuel is crucial to environmental safety.

The combination of radiation and organic contamination may lead on the one hand to radiation induced defects on the surface, and on the other hand to amorphous carbon formation which can influence the reaction of gases with the uranium surface. The amorphous carbon on top of nuclear materials may be the product of decomposition under radiation of hydrocarbons participating in machining of fuel elements or even atmospheric origin adsorbed hydrocarbons or CO_2.

In earlier publications [5,6] it was demonstrated that an amorphous carbon layer, deposited by either applying plasma of $CH_4 + Ar$ mixture or thermal evaporation, significantly enhances the interaction of hydrogen with the uranium surface. Fig. 1 [6] demonstrates the preferential hydrogen attack (forming uranium hydride) on the carbon covered area of the naturally oxidized uranium metal.

Two possibilities discussed [6] for this enhanced reaction were (i) Change of the oxide due to reaction with the deposited carbon, either during the long time of close contact or during the preheating, as part of the experiment (desorption of random surface groups), or (ii) Enhanced dissociation of hydrogen on top of the carbon layer or at the carbon/oxide interface.

In the present experiment, a few nm thick carbon layer was deposited by thermal evaporation on half of a sample of stoichiometric polycrystalline thin film (~100 nm) of UO_2 prepared by sputter deposition, while the other half was masked and kept uncovered, for comparison.

Exposures to D_2 gas (to differentiate from humidity dissociation hydrogen) and measurements of its effects were performed, in order to study the influence of the deposited carbon layer on the interaction of the D_2 with the dioxide layer, in order to understand the enhanced hydrogen attack on U metal under a native oxide, studied in the previous experiments.

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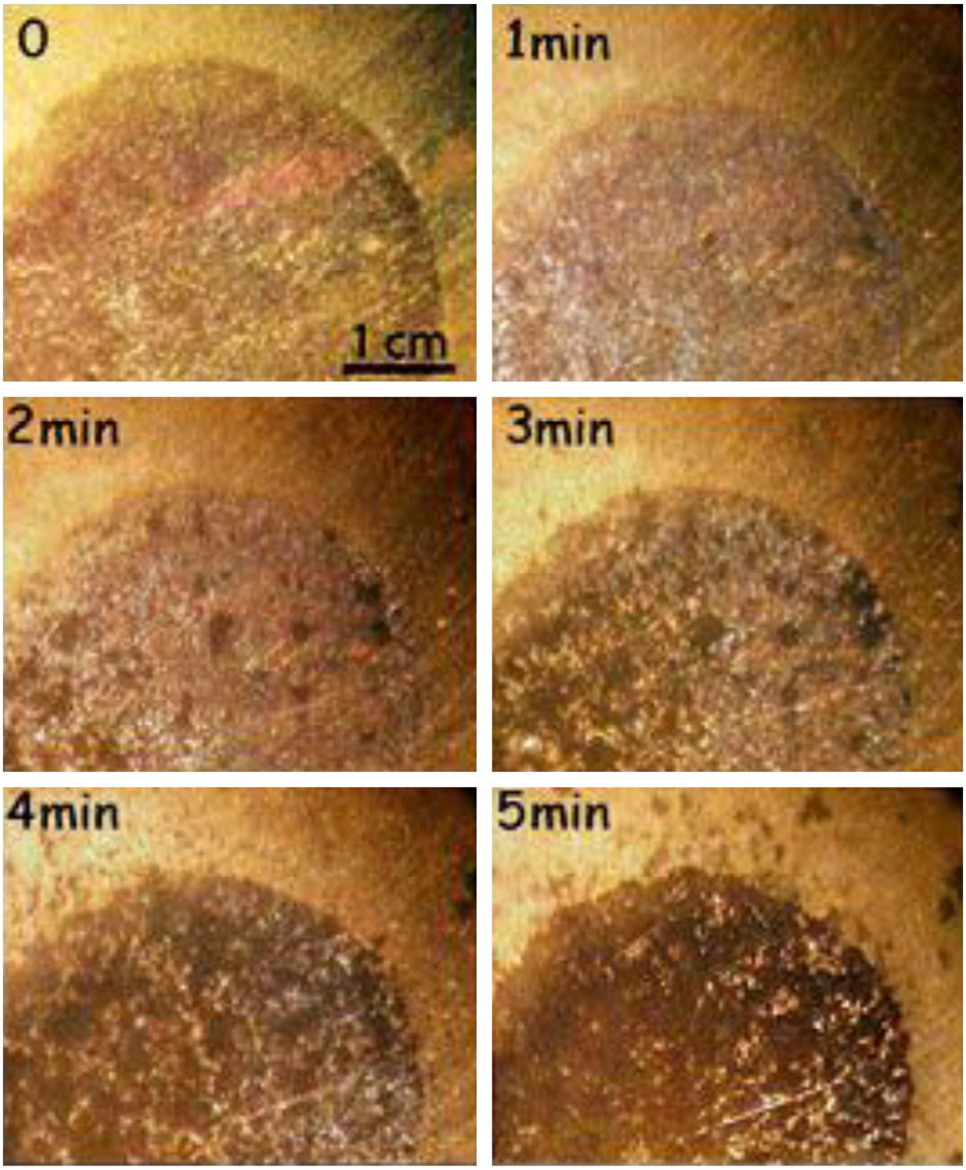

Fig. 1. [6]: HSM micrographs, taken during the exposure of native oxide covered uranium, to hydrogen, at 90 °C and 14.6 PSI, presenting the preferential hydrogen reaction with the carbon covered area of the oxidized uranium surface.

Experimental

Sample preparation

Stoichiometric polycrystalline thin films (~100 nm) of UO_2 were prepared at the Institute for Transuranium Elements (ITU) by direct-current sputter deposition from native U metal with Ar/O_2 mixtures, as sputter and reaction gas. The films were deposited onto a Mo foil substrate (~1 cm^2 area, 1 mm thickness) cleaned in situ with Ar^+ ions while heated to 570 K for at least 25 minutes before deposition. The plasma in the diode source is maintained by injection of electrons of 50–100 eV energy. This allows a low sputter gas pressure of down to 10^{-2} Torr. The Uranium metal target was held at −800 V while no sample bias was applied. The background pressures in the preparation and analysis chambers were below 2.7×10^{-8} and 4×10^{-10} Torr, respectively. X-ray diffraction (XRD), Ultraviolet photoelectron spectroscopy (UPS), and X-ray Photoelectron Spectroscopy (XPS) characterizations of the sample after preparation showed clean surface with calculated O/U ratio of 2.02.

A very thin (few nm) carbon layer was deposited by thermal evaporation on the sample, half of which was masked, leaving a UO_2 surface, for comparison measurements.

Experimental procedure

The sample was transferred to a UHV system equipped with X-ray Source XR50 and Hemispherical Energy Analyzer PHOIBOS 150 MCD (both SPECS) and heated to 570 K on the sample holder containing a Boralecrtic heater followed by D_2 exposure at RT. Composition and chemical bond-configuration at the near-surface region at each stage of the experiment was investigated by XPS using AlKα radiation as excitation source (1486.6 eV). Small spot XPS measurements of the carbon covered and bare UO_2 surfaces were carried out using Small Area Lens Mode and 7:3 Exit Slit of the Analyzer. The sample was then transferred (in ambient conditions, humidity 50–60%) to the SIMS system, for analysis. This procedure is similar to the transfer of the samples in the earlier studies [5,6] to the reaction chamber.