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Development of fuel-model interfaces: Investigations by XPS, TEM, SEM and AFM

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ABSTRACT

The presented work aims to reproducibly prepare UO_2–Pd thin film model systems for spent nuclear fuel in order to further investigate surface reactions of these films under relevant redox conditions. The sputter co-deposition of U and Pd (fission product) in the presence of O_2 results in the homogenous distribution of Pd in a crystalline UO_2 matrix. Heating the films causes the diffusion of film components. Hereby, the formation of ε-particles has to be clarified. First electrochemical studies show the influence of the nobel metal Pd on the redox behaviour of UO_2. With increasing Pd concentration the matrix dissolution is decreased. However, we could demonstrate that blocked oxidation processes are of temporary nature. The passivation of the Pd reactive sites with increasing number of cycles finally induces the approximation of the mixed system to the redox behaviour of the pure UO_2 system.

1. Introduction

The principal concern in nuclear waste disposal is the possible leaching of radionuclides into the groundwater and the associated risk of ecological and human exposure. In this context, investigations of the mechanisms of spent nuclear fuel corrosion, which possibly results in radionuclide release into the groundwater, are of main interest. Spent nuclear fuel mainly consists of UO_2 (~95%). The remainder is a mixture of fission products, transuranium elements and activation products that occur in many different forms such as gases, oxide precipitates, solid-solutions or immiscible, micron- to nanometer-sized metallic precipitates of Mo, Tc, Ru, Rh and Pd (ε-particles). Due to the rapid consumption of environmental oxidants in the near field of a nuclear waste repository, radiolytic oxidants will have a primarily influence on fuel corrosion [1]. Since the fuel will not be wetted while γ/β radiation fields are significant [2] only the effects of α-radiolysis are considered responsible for its corrosion. The influence of α-radiolysis on the corrosion of UO_2 has been extensively studied by several authors and a number of models have been proposed to predict its influence on radionuclide release [3–10]. In all these studies α-radiolysis is supposed to produce oxidants, once groundwater wets the fuel surface:

$$H_2O \xrightarrow{\alpha} {}^{\cdot}OH, e^-, {}^{\cdot}HO_2, H_2O_2.$$

The oxidizing species are taken up by the fuel surface, and additional oxygen atoms enter the UO_2 structure as interstitial oxygens. As a result, the fuel reaches a composition of UO_{2+x}, with x ranging between 0.3 and 0.4. The thus generated U(VI) at the fuel surface is then dissolved. Ungoing dissolution finally results in the precipitation of secondary U(VI)-phases under oxidizing conditions.

Another important process in the direct environment of the fuel that counteracts the oxidation of the UO_2 matrix is the generation of the reductant H_2 by corrosion at the steel surface [11]:

$$Fe + 2H_2O \longrightarrow Fe^{2+} + 2OH^- + H_2$$

Spent fuel leaching studies in the presence of H_2 have shown it to have a very strong influence on radionuclide leaching and fuel corrosion rates [12] which are reported to be decreased by about four orders of magnitude in the presence of hydrogen [13]. The mechanisms that could explain the effect of H_2 can be generally subdivided in homogeneous reactions in solution or heterogeneous reactions at the solid-solution interface. Homogeneous reactions involve the consumption of radiolytically produced oxidants by H_2 as well as the reduction of of dissolved U(VI) itself. The decomposition of H_2 at the fuel surface (heterogeneous reaction) would result in the production of $H^{\cdot}$ radicals which subsequently reduce the fuel matrix. Up to now it is not entirely clear which component of the surface is responsible for the activation of hydrogen or if different components such as the UO_2(s) matrix itself [14], transuranium oxides [15] or metallic inclusions (ε-particles) [16,11] act together regarding the decomposition of hydrogen.

This study focuses on the influence of nobel metal inclusions (ε-particles) on the UO_2 redox behaviour. To this aim, we use thin layers of UO_2 doped with Pd in order to simulate the most simple system for spent fuel. The thin film technique allows an easy and controllable way to produce representative samples of the desired elemental composition by the use of small amounts of starting

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materials such as elemental uranium or palladium [17]. Another advantage of this technique is the accessibility of thin films to surface analysis tools which allow the 1) characterization of surface properties as well as 2) the monitoring of surface reactions such as electrochemical processes.

According to point 1) the objectives of the presented work is to first prepare thin films in a reproducible manner and to fully describe their properties with regard to generate model systems that exhibit the same physico chemical features as spent fuel. In a next step (point 2)) the redox chemistry of the 'quasi real' surface is studied.

2. Experimental

Thin films of $U_xO_yPd_{100-x-y}$ were prepared in situ by sputter co-deposition from U (99.9% purity) and Pd (99.9% purity) targets at a O_2 partial pressure of about $1 * 10^{-6}$ mbar. The pressure of the sputter gas (Ar 99.9999% purity) was $1 * 10^{-2}$ mbar. In order to get an Ar-plasma, the Ar atoms were ionized by electrons (50–100 eV) emitted from a hot W cathode. The composition of the $U_xO_yPd_{100-x-y}$ films was controlled by the respective target voltages as well as the oxygen partial pressure. Deposition rates were about 0.5 monolayers per second. The thickness of the films was checked by weight difference before and after sputter deposition.

Depending on further experimental treatment of the surfaces, various film–substrate systems were used in this study. For the surface analysis by XPS, films of 10 nm thickness were deposited on single crystalline Si-wafers. Since the sputter source is mounted in the preparation chamber which is separated from the analysis chamber (background pressure $2 * 10^{-10}$ mbar) of the photoemission spectroscope the in-situ preparation of samples without contamination of the analysis chamber, and direct transfer to the spectrometer for surface analysis is possible.

For the topographic characterization of the thin films layers of about 1 µm thickness were deposited on polycrystalline gold discs (10 mm in diameter, 0.25 mm thickness, 99.99% purity) and measured ex-situ with a commercial AFM (Topometrix, TMX 2000, Explorer). The same samples were measured with a scanning electron microscope (Philips ESEM XL 30 FEG) equipped with a backscatter electron detector for imaging. XRD measurements (Philips PW3830 X-ray generator fitted with a Philipps PW 2213/20 goniometer) were done ex-situ with films of 1 µm thickness deposited on single crystalline Si-wafers. TEM measurements (TEM H700 HST from Hitachi; ex-situ) required the deposition of 120 monolayers (36 nm thickness) onto Cu-grids coated with carbon. In order to perform combined cyclovoltammetric and mass change measurements (ECQM), thin films of about 1 µm thickness were sputtered onto a working electrode, represented by oscillating quartz crystals with a Au-deposition on each side. ECQM measurements were then performed ex-situ with a CH Instruments Model 430 Electrochemical Quartz Crystal Microbalance.

3. Results and discussion

3.1. Characterization of UO_2-Pd thin films

Thin films were prepared by sputter co-deposition from elemental uranium and palladium targets in the presence of oxygen. The surface composition of the sputtered films was determined by analyzing the U 4f / Pd 3d area ratios of the corresponding XPS spectra (Fig. 1a). It could be shown that the systematic variation of target currents reproducibly controls the concentration of the Pd-inclusions which ranges from 2% (detection limit) to 90% (cross-contamination with U). Fortunately, the shape of the U 4f peak in the XPS spectrum of U allows identifying its oxidation state and with this allows determining the needed oxygen pressure for the generation of UO_2 in a qualitative manner (Fig. 1b).

The co-deposition of uranium and palladium results in the formation of UO_2-Pd agglomerates ~100 nm in size as could be shown by AFM imaging. XRD and TEM measurements confirm the crystalline nature of these agglomerates. SEM as well as TEM investigations indicate the homogeneous distribution of Pd in the UO_2 matrix. Hereby, at low Pd concentration the incorporation of the nobel metal gives rise to its oxidation as can be deduced from the interpretation of the corresponding XPS spectra (Fig. 2) [18–20]. By contrast, at higher Pd concentration the XPS spectrum can be attributed to metallic Pd (Fig. 2). At the same time XRD and TEM measurements exhibit the loss of crystallinity of the UO_2 matrix and with this indicate the dispersion of uranium oxide in the metallic Pd phase instead.

In order to generate palladium ε-phases in a crystalline UO_2 matrix, sputtered UO_2-Pd films were heated in several steps (from room temperature to ~840 °C) after deposition. The corresponding XPS overview spectra are shown in Fig. 3. The continues change of

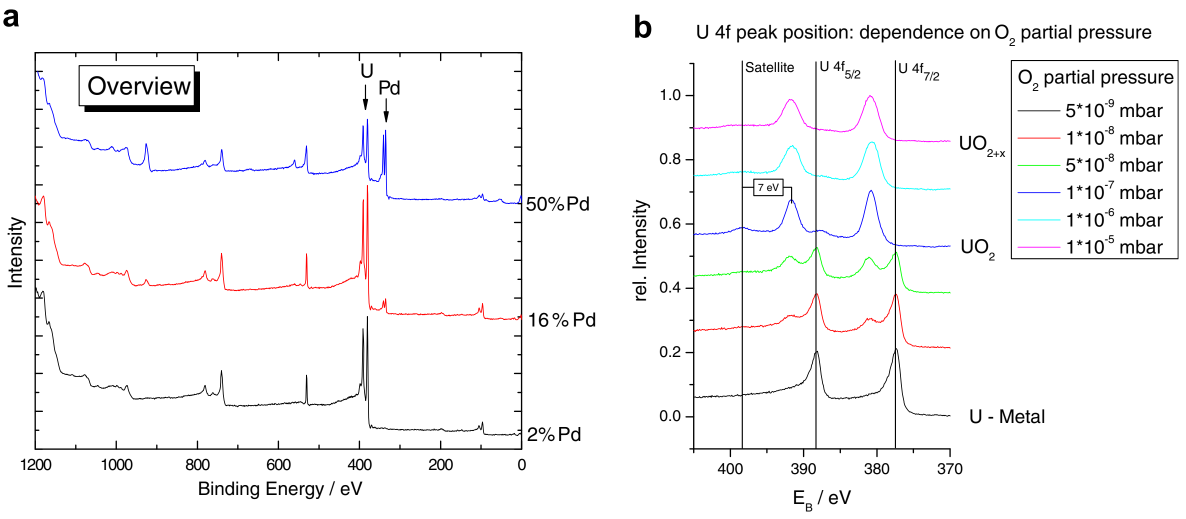

Fig. 1. (a) XPS spectra of a fuel-model interface prepared by sputter co-deposition of U and Pd in presence of O_2. The variation of target currents results in a varying concentration of Pd incorporation. (b) U 4f spectra of U sputtered at different O_2 partial pressures. UO_2 is generated at $1 * 10^{-7}$ mbar O_2.

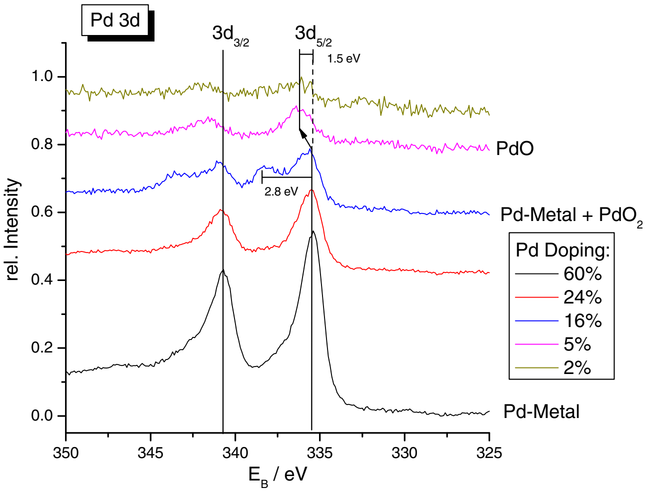

Fig. 2. Pd 3d spectra of UO_2 thin films with increasing/decreasing Pd doping concentration. Depending on the Pd concentration the nobel metal is partly oxidized.

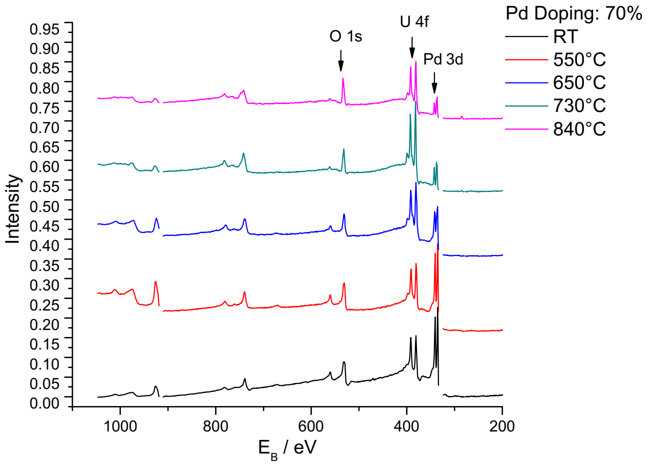

Fig. 3. XPS overview spectra of a thin film composed of UO_2 doped with 70% Pd. Heating the film up to 840 °C after deposition results in a change of its composition.

the U/Pd ratio with increasing temperature is striking. Obviously, the thin film components are no longer fixed in their matrix positions and start to change their structural arrangement. The increase of U concentration as compared to Pd indicates its diffusion to the surface or rather the Pd depletion of the surface perhaps by Pd diffusion into the Si-wafer.

It has to be clarified if such diffusion process finally results in the formation of ε-particles.

3.2. Surface redox-reactions

As it is indicated in the introduction we are interested in the influence of the nobel metal Pd on the redox behaviour of UO_2. To this aim, we investigated cyclovoltammetric (CV) measurements of a series of UO_2 thin films doped with different amounts of Pd inclusions (characterization by XPS). Since the oxidation of UO_2 results in its dissolution whereas UO_2^{2+} reduction results in the precipitation of the uranium oxide, the mass changes during the different redox cycles were monitored by ECQM (Electrochemical Quartz Crystal Microbalance).

The transfer of samples after co-deposition to the ECQM apparature results in the oxidation of the first layers of the film surface.

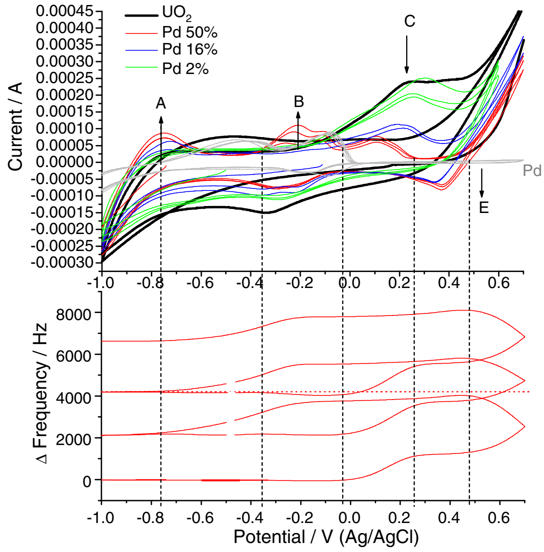

Fig. 4. Cyclovoltammograms of UO_2 thin film model systems doped with 2%, 16% and 50% Pd. For a better interpretation of the redox data the corresponding ECQM diagram of the 16% Pd sample is also shown.

We therefore did run a reductive scan before measuring the CV. The cyclovoltammograms of a series of films are shown in Fig. 4 together with the ECQM diagram of the thin film with 50% Pd inclusion.

The redox behaviour of a UO_2 film doped with 2% Pd resembles that one of the pure uranium dioxide. This changes with increasing Pd concentration in the UO_2 matrix. New features appear in the cyclovoltammogram (region B and E) whereas others disappear (region C). The increase of current in region B is due to an oxidation process which is accompanied by a decrease of frequency (increase of mass) in the ECQM frequency plot. Obviously, the oxidation process is equatable to an incorporation of O^{2-} and we assume the formation of higher uranium oxides. The finestructure of the peak indicates that also Pd is involved in this oxidation process (reference CV of Pd given in the diagram). The typical oxidation feature in region C decreases with increasing Pd concentration and is shifted to lower potentials. The corresponding part in the ECQM plot clearly shows an increase of frequency. With this, the feature in region C can be attributed to an oxidative dissolution of the matrix which is inhibited at higher Pd concentration. However, we could demonstrate in another experimental series (not shown here) that such an inhibition of surface oxidation only lasts for the first few redox cycles. With increasing number of cycles the Pd reactive sites are passivated and the electrochemical features, including dissolution properties, resemble more and more the pure UO_2 system. The feature in region E can be attributed to a reduction process which is accompanied by the precipitation of secondary phases (increase of frequency in the ECQM diagram) already at 0.4 V in contrast to – 0.3 V for the pure UO_2 system. Studies are under way to characterize these secondary phases.

The intention of the presented study was first to simulate the most simple system for spent nuclear fuel by preparation of UO_2-Pd thin films which exhibit the same physico chemical features as the technical fuel analogon. The characterization of the prepared films clearly show that the formation of a crystalline UO_2 matrix is feasible. The formation of ε-particles in such a matrix still has to be clarified. First electrochemical studies clearly show the influence of nobel metals such as Pd on the redox behaviour of UO_2. Obviously the dissolution of the UO_2 matrix is decreased with increasing Pd concentration. In order to characterize the Pd catalytic properties the interaction of Pd and H_2 are investigated in a next set of experiments.

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