РЕЗЮМЕТА НА ОСНОВНИТЕ РЕЗУЛТАТИ И НАУЧНИТЕ ПРИНОСИ НА АНГЛИЙСКИ

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ЗА УЧАСТИЕ В КОНКУРС ЗА АКАДЕМИЧНА ДЛЪЖНОСТ „ ДОЦЕНТ “

1. Habilitation thesis (papers 1-6)

1.1 Modelling the growth and restructuring of oxide films on structural materials from the first loop of nuclear power plants

Based on the mixed conductivity model, the corrosion processes occurring on the first loop surfaces of nuclear reactors have been quantitatively described (Paper 1). A combination of in-situ impedance spectroscopy and ex-situ characterization of the thickness and chemical composition of the oxide layers with XPS has been used for the experimental characterization of these processes. The depth profiles of the metal components of the inner, continuous oxide layer on a structural material during its growth are represented by the dependences of the corresponding atomic fractions on the distance to the alloy/inner layer interface. Unsteady diffusion and migration equations for each component, solved at appropriate initial and boundary conditions, are used to calculate these profiles. The growth of the outer, deposited oxide layer is considered as a diffusion process in a matrix composed of the crystallites of this layer and the heat carrier between them. Thus, a system of unsteady diffusion equations is used to calculate the profile of the corresponding metal component. The boundary conditions at the interface between the crystallites of the inner layer and the outer layer are identical to those at the interface between the inner layer and the heat carrier, which ensures continuity of the oxide film composition on the structural material. The resulting The objective was to use a quantitative procedure to interpret the electrochemical impedance and surface analyses to obtain estimates of the oxidation rate constants of the individual alloying elements (Ni, Cr and Fe), the diffusion coefficient of oxygen vacancies, and the field strength in the growing oxide. The main conclusion is that increasing the concentration of LiOH in the simulated hot-dipping conditions leads to higher dissolution, metal oxidation and transport rates in the oxide, or in other words, the formed oxide is more perfect. On the other hand, the addition of H_3BO_3 has a beneficial effect that counteracts the accelerating influence of Li. An optimal aqueous-chemical

hot-dipping regime with low to medium Li content and B addition was proposed, which leads to the growth of layers with better electrochemical stability and corrosion resistance (Paper 2).

1.2 Influence of water chemistry regime on fuel cladding corrosion in pressurized water nuclear reactors

A quantitative model of the corrosion of zirconium alloys as fuel claddings of nuclear power plants has been developed, quantifying both the processes during the stable growth of the protective oxide layer and the transitions between two periods (Papers 3 and 4). To develop, validate, and verify the model, long-term in-situ electrochemical measurements during oxide layer growth have been conducted in simulated first-loop water chemistry regimes of pressurized water power plants, from which a database of the corrosion behavior of the in-shell materials has been established. For this purpose, a laboratory re-circulation loop was designed, built and commissioned to conduct electrochemical measurements at temperatures up to 350 °C and pressures up to 15 MPa. It consists of a low-temperature part for the control of the water-chemical regime and a high-temperature part with a measuring autoclave in which the elements of a three-electrode electrochemical cell are located. The developed kinetic model of fuel cladding oxidation in a first-loop heat carrier is based on the conjugate currents approach and the mixed conductivity model, taking into account the influence of internal oxide stresses and the spatial loading of point defects and aliovalent alloy impurities on the values of transport parameters (diffusion coefficients and electric field intensity). Based on the model, equations for the oxide thickness growth and the amount of incorporated hydrogen as a function of time, temperature and water-chemical regime are derived. The effect of irradiation on the alloy was simulated by pre-situ and ex-situ electrochemical incorporation of protons into it under cathodic polarization. The model was validated by quantitative comparison with laboratory and operational data for pressurized water plants. Software has been developed for the application of the model, which has been implemented at Kozloduy NPP in 2021.

1.3 Mechanism of corrosion erosion and sludge formation in the second loop of nuclear power plants

The corrosion erosion of carbon steel in the pressurized water heat carrier of the second loop of nuclear power plants has been investigated by impedance spectroscopy in the temperature range 100-240 °C at a pressure of 9 MPa and a heat carrier inlet flow rate of 4-10 $dm^3\ h^{-1}$ (Paper 5).

The hydrodynamic calculations show that the developed flow cell with accelerating insert provides linear flow velocities up to 1 m s^{-1} and Reynolds numbers above 10^4, i.e. the typical turbulent conditions for the process are reached. The influence of the flow rate on the corrosion potential is in agreement with thermodynamic predictions of a change in the stable corrosion product with increasing temperature (from $FeOH^+_{aq}$ in the 100-160 °C range to magnetite at higher temperatures). The influence of the flow rate on the impedance spectra is negligible, implying that the corrosion rate is limited by the processes of load transfer and defect transport in the oxide rather than by convective transport of corrosion products in the heat transfer medium. The results are interpreted with a quantitative kinetic model involving two parallel processes, oxide growth and dissolution with a colloidal magnetite end product soluble iron ions (probably $FeOH^+$) (Paper 5). The model was calibrated with the oxide thickness at the oxidation end estimated by galvanostatic reduction. The model was parameterized by a complex nonlinear regression of the experimental impedance spectra to the corresponding temperature-dependent transfer function (100-240 °C). Based on these calculations, equations for the oxide growth rate and soluble corrosion product release are derived. The temperature dependence of the corrosion erosion rate under these conditions is expressed by the reciprocal of the charge transfer resistance at the oxide-thermal interface and passes through a maximum between 160 and 180 °C. Software for the application of the model has been developed and implemented at Kozloduy NPP in 2021.

Based on a preliminary assessment of the electrical properties of magnetite particles in the heat transfer fluid, a quantitative model of slurry formation and consolidation depending on the water chemistry regime in a second loop was developed, parameterized, validated and verified (Paper 6). To verify the model, experiments were carried out to quantify the kinetics of magnetite deposition on AISI 316 steel in the second-loop aqueous-chemical regime using electrochemical impedance spectroscopy at different temperatures, which characterized the initial stages of the process very well. Parameterization of the proposed model was accomplished by quantitatively comparing the experimental data with the transfer function of the mixed conductivity model. The magnetite-time filling rate curves were quantitatively compared with the basic kinetic equation of the proposed model, and reliable estimates of the rate constants of magnetite particle deposition, separation, and consolidation were obtained. The rate constants increase with temperature, with this increase being the least pronounced for the consolidation constant, most likely related to the higher mobility of iron ions leading to a weaker consolidation trend at higher temperatures. The model predictions are compared with literature data from laboratory experiments and operational data, and conclusions are drawn

about its applicability for quantifying slurry deposition and consolidation kinetics of sludge deposition and consolidation. Software for the application of the model has been developed and implemented at Kozloduy NPP in 2021.

2 Scientific publications outside the habilitation thesis

2.1 Modelling the formation processes of barrier oxide films on niobium and tungsten

A quantitative kinetic model including the processes of film growth/dissolution into and metal dissolution through the oxide as parallel process pathways quantitatively reproduces the steady-state current-potential curves and impedance spectra for W and Nb over a wide range of potentials and pH (Paper 7). The pseudoinductive time constant in the spectra at intermediate frequencies is explained by the interaction between current carriers of opposite sign, which accelerates the transport of the fundamental current carrier in the nonstationary regime. The model is also found to reproduce quantitatively the experimental estimates of the surface atomic parts of W(V) and W(VI) and the film thickness versus potential. Based on this model and recent theories on the effect of stress and strain on the anodic oxidation of metals in film-dissolving electrolytes, a conceptual model of the nanopore initiation process was created. According to this approach, the interaction between surface energy perturbation and spatial separation and electrochemical metal dissolution leads to surface instability and pore nucleation. The preferential dissolution from the concave and the corresponding film growth on the convex regions promotes the deepening of the nanopores. The electrostatic repulsion due to the accumulation of cation vacancies in the pore walls as a result of electrochemical dissolution acts as a driving force to separate the nanopores to form nanotubes. Evidence for this concept is presented based on characterizing the conduction mechanism of nanoporous films with ex-situ impedance measurements in a non-dissolving film electrolyte (Paper 7).

2.2 Modelling the formation processes of anodic oxide films on titanium and titanium alloys

The processes at the Ti/H_2O interface were investigated by performing DFT simulations to estimate the adsorption energy of the water molecule as a function of its orientation on the surface (Paper 8). For this purpose, a water molecule in three different orientations, surface (top), hexagonal dense packing (hcp) and wall centered cubic (fcc), was adsorbed on the surface

of a five-layer model of the titanium surface. The changes in the energy of the molecule as well as the change in its geometry due to adsorption were evaluated. Results for Ti(0001) show that the water molecule is most stable in the hcp position parallel to the 'a' axis. In this orientation it is characterized by the highest adsorption energy (-0.632 eV). The corresponding values for the other two orientations of titanium are top (10-10, -0.975 eV) and fcc (11-20, -0.899 eV). Quantitative information on the reactivity of different crystallographic planes of Ti with respect to water adsorption was obtained, and the effect of applied potential on adsorption was quantitatively characterized (Paper 10). It can be concluded that in the investigated range of potentials, including the zero-load potential, dissociative adsorption of water molecules with the formation of H_{ad} and OH^- is observed on the titanium surface. There is a gradual oxidation of the surface layer by titanium atoms due to successive adsorption of OH^- and O_{ad}, as the variation of free energy of adsorption of these particles is significantly higher compared to that calculated for other metals. A quantitative deterministic model of the growth of oxide films on titanium in fluoride-containing electrolytes has been parameterized by quantitative comparison with various types of electrochemical data (current-potential curves, electrochemical impedance spectroscopy, and dynamic impedance), photocurrent transients, and photocurrent energy spectroscopy, combined with ex-situ oxide surface composition data obtained by X-ray photoelectron spectroscopy (Paper 9). For the first time, in-situ photocurrent-time curves for the Ti/TiO_2/ EG-H_2O-NH_4F system were successfully measured over a wide range of fluoride potentials and concentrations (Papers 9 and 10). The results allow to estimate the rate constant of the ion defect recombination reaction at the film/solution interface depending on the applied potential and the fluoride content in the electrolyte. Using dynamic impedance measurements at high frequencies, the increase in oxide thickness with time was evaluated as a function of the main oxidation parameters, applied potential and fluoride ion concentration. The rate constants and transport coefficients that characterize the oxide growth, dissolution and pore formation at the oxide/electrolyte interface. Combining different electrochemical and physical methods allows for extending the validity of the model to lower fluoride concentrations and higher applied potentials, and gives a deeper insight into the evolution of the system after several hours of polarization. The main processes at the titanium oxide-solution interface (adsorption of water molecules and fluoride anions) are modeled by DFT+U simulations. The model has been extended to quantitatively describe the growth and dissolution of anodic films on Mo in concentrated phosphoric acid, and its parameterization has been accomplished by quantitative comparison of model calculations with experimental data on current-potential curves, impedance spectra, photocurrent, and layer chemistry estimated by XPS (Paper 10).

A comparison of the anodic oxidation of a titanium alloy (Ti-15%Mo-3%Nb-3%Al) with that of pure titanium in an ethylene glycol-water-fluoride electrolyte has been made by electrochemical impedance spectroscopy, photocurrent transients, photocurrent energy spectroscopy, photocurrent spectroscopy with light intensity modulation, and surface analyses (Papers 11 and 12). Experimental data from all the methods used are quantitatively reproduced across a wide range of applied potentials using a kinetic model previously proposed for pure Ti. At an applied potential of 2 V, the currents for the alloy are significantly higher than those for pure Ti, while for potentials above 4 V, the currents for Ti are higher. This may indicate less influence of the applied potential on the corresponding oxidation stages of the alloy compared to pure Ti. The maximum photocurrent for the oxide formed on the alloy is significantly lower than that for pure Ti. The decrease in photocurrent with time is related to a current carrier recombination process that is more efficient for the oxide formed on the Ti alloy. After a certain oxidation time, a secondary layer begins to grow on the barrier film and the processes within it are probably responsible for the recombination of electron carriers. The oxide thickness on pure Ti is less than that on the alloy at potentials lower than 6 V, while at higher potentials an inverse dependence is observed. The oxidation/dissolution rates near the steady state are lower for the alloy compared to pure titanium. The initial value of the dissolution rate constant of the barrier layer is higher for the alloy, but its rate of decrease is also greater, so that the steady state is reached at lower dissolution rates. Overall, it can be concluded that the oxide film on the alloy provides a better barrier against corrosion and dissolution, but possesses inferior electronic properties than that on pure Ti.

2.3 Synthesis and modification of steel and titanium oxides as photocatalysts for water decomposition

The in-depth oxide film chemistry, electrochemical and photoelectrochemical properties of anodic oxides formed by different methods (galvanostatic, mixed, tensiodynamic + galvanostatic and potentiodynamic + potentiostatic) on stainless steel in ethylene glycol fluoride electrolytes with low water content were quantitatively characterized (Paper 13). The surface oxides are shown to contain only iron in the trivalent state, while oxygen is mainly present as O_2^- , and the stoichiometry is close to Fe_2O_3. The oxides have a bilayer structure, with the inner layer enriched in Cr, Mo and Mn, while the outer layer contains predominantly Fe, with some Mn and Cu present. A maximum concentration of Ni is observed at the film/alloy interface. Electrochemical characterization by EIS shows that oxides formed galvanostatically in a short time are more defective than those formed in tensiodynamic + galvanostatic and

potentiodynamic + potentiostatic modes. Quantitative interpretation of impedance spectra with a transfer function at the semiconductor/electrolyte interface indicates the presence of surface states, especially in oxides formed galvanostatically in a short time. The photocurrent energy spectra show that the oxides absorb light throughout the visible spectrum, with an approximate indirect forbidden zone width of about 1.8-2.0 eV, i.e., slightly lower but comparable to that of hematite. Photovoltammetry demonstrates significant modulated photocurrents already at low potentials in the region where the donor state appears in the capacitance-potential curves. A generalized transfer function was used to quantitatively interpret the intensity-modulated photocurrent spectra (IMPS), and good catalytic properties of the oxides were found, especially when a hole trap, hydrogen peroxide, was added to the solution. In the absence of peroxide, load transfer at the interfacial interface is slow and recombination is very efficient. This type of oxides can be converted into highly efficient catalysts for photoassisted water decomposition electrodes by further modification. Nanoporous titanium dioxide doped with molybdenum oxide was successfully synthesized and characterized in terms of its thickness, chemical composition, electrical, electrochemical and optical properties (Paper 14). The combined galvanostatic and tensiostatic method was suitable for the preparation of nanoporous titanium oxide samples by anodic oxidation in a range of ethylene glycol-based solvents containing water and ammonium fluoride. The porosity of the oxides was estimated on the basis of re-anodization (pore filling), generally decreasing with increasing oxidation time and applied voltage and not significantly dependent on the fluoride and water concentrations in the electrolyte. The optical characteristics of the nanoporous oxide samples show absorption predominantly of UV light, although weak absorption in the visible region is also observed, probably due to doping of the oxides with carbon, nitrogen and fluoride. The deposition of molybdenum oxide in the TiO_2 matrix by a potentiodynamic method results in almost complete coverage of the surface with molybdenum oxides. The maximum penetration depth is comparable to the thickness of the nanoporous matrices, indicating effective pore filling. The XPS results indicate the formation of mixed valence molybdenum oxide in which the oxidation state of Mo(V) dominates, the Mo(VI) content is significant while Mo(IV) is in less amount. Quantitative interpretation of electrochemical impedance measurements shows that the rate of the anodic process is limited by the transport of electron current carriers through the oxide, which is typical for semiconductor electrodes under depletion conditions. Deposition of Mo oxide in nanoporous TiO_2 matrices significantly enhances light absorption in the visible region, i.e., the resulting oxides are promising candidates for photocatalytic applications such as water decomposition. The dynamics of photoinduced photocurrents in porous anodic TiO_2 modified

with Cu_2O by pulsed electrodeposition have been investigated at steady state and by modulated photocurrent measurements over a wide range of experimental conditions (Paper 15). Pulsed electrodeposition of Cu oxide on nano-porous anodic TiO_2 leads to efficient surface coverage (up to 60 % Cu) under optimal synthesis conditions (60 ◦C, 60 min, lower pulse potential -0.55 V). The copper oxide is of mixed valence, containing mostly Cu(I), a small amount of Cu(II) and its stoichiometry is close to Cu_2O. In this case, the stationary current densities under illumination are 6-7 times higher than those in the dark, indicating photocatalytic activity of the oxides with respect to water reduction with hydrogen evolution. The quantum yield of the modulated photocurrent is maximal for films formed in 15-30 min at -0.55 V/ 60◦C. It increases during polarization at -0.6 V in 0.1 M KOH. The indirect width of the forbidden zone of the photoactive oxide phase is about 2.0-2.2 eV in agreement with literature data for Cu_2O. Measurements of photocurrent spectra with light intensity modulation in 0.1 M KOH over a wide potential range for films formed under different conditions (temperature, electrodeposition time, and lower pulse potential) are consistent with a generalized model of load transfer and recombination. The quantitative interpretation of the spectra using the corresponding transfer function allows one to estimate the formal rate constants of charge transfer and recombination as a function of light potential and energy. The highest values of these constants were found for films formed at 60◦C for 1 h at a lower pulse potential of -0.55 V, indicating that the photocatalytic activity of these films is highest.

2.4 Online NobleChem simulation in fluidized bed nuclear reactors

Online NobleChem is a technology to reduce stress corrosion cracking of in-shell materials in fluidized bed nuclear reactors. To more effectively reduce the corrosion potential under hydrogen water chemistry conditions, solutions of noble metal salts (e.g. Pt) are dosed into the feed water during reactor operation. It is claimed that they are deposited as very fine metal particles on all surfaces in contact with the coolant and retain their electrocatalytic properties over long periods of time. To investigate the deposition and redistribution behaviour of Pt, a laboratory loop was developed to simulate a high-temperature steam-water cycle in which specimens could be exposed to a simulated Pt-containing heat carrier (Work 16). The samples were analyzed by inductively coupled plasma-mass spectrometry and laser sputtering (LA-ICP-MS). The results of experiments with different dosing rates of the same amount of Pt showed a faster and more pronounced decrease in corrosion potential and a slightly larger average Pt particle size at using a higher injection speed. Longer preoxidation of the samples seems to increase the average Pt concentration on the material surface. Based on corrosion potential

measurements, scanning electron microscopy and LA-ICP-MS analyses, it can be concluded that Pt deposition is more efficient at higher rates, resulting in lower potential and therefore better protection against stress corrosion cracking. On the other hand, at lower doping rates, some Pt nanoparticles are hidden under large crystals of the outer oxide layer, while others incorporated to a depth of 5-10 nm in the inner oxide layer. These observations help to explain the less effective reduction in corrosion potential.