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DELIVERABLE (D-N°: 2.2)
Status of Rim and Grain Boundary Diffusion Experiments (34 months)

FIRST-Nuclides

(Contract Number: FP7-295722)

D.H. Wegen, P. Carbol, H. Curtius,
J. Vandenborre

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Status of Rim and Grain Boundary Diffusion Experiments (34 months)

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Objectives

The second component "Rim and grain boundary diffusion" of work package 2 (WP2) deals with investigations on oxygen diffusion in spent UO_2 fuel. The examination of diffusion mechanisms will result in the quantification of water penetration into the fuel (grain and grain boundaries) structures and subsequently couple the diffusion/corrosion phenomena. Furthermore, investigations on irradiated and unirradiated fuel kernels separated from high temperature gas cooled reactor (HTR) fuel have been performed which are complementary to those on light water reactor (LWR) fuel. The experimental part of WP2 started in project month 4 and will end in project month 36 [1], [11].

The JOINT RESEARCH CENTRE – INSTITUTE FOR TRANSURANIUM ELEMENTS (JRC-ITU) is the leading organization of WP2. The investigation of diffusion effects started in the first project year with the characterisation and preparation of spent fuel samples, which will be used for corrosion experiments in $H_2{}^{18}O$ water at room temperature. It was planned to determine the $^{18}O/^{16}O$ depth profiles using a shielded SIMS (secondary ion mass spectrometry) to quantify the oxygen diffusion into spent nuclear fuel (SNF).

FORSCHUNGSZENTRUM JÜLICH GMBH (JÜLICH) is working on spent high temperature reactor fuel. Within the first half of the project the radionuclide inventory in the fuel kernel and in the coatings were determined and compared to calculated values as well. Further on investigations of the microstructure and of the elemental distribution of the fuel kernel and of the coatings are performed before (first half of the project) and after leaching (second half of the project). After cracking of the tight coatings the fission gas release fraction was measured in the first 18 months. Then static leaching experiments with the separated fuel kernels and coatings were started in 2013 in order to determine the fast instant radionuclide release fraction.

Unirradiated tristructural-isotropic (TRISO) fuel particles are investigated by the CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (CNRS) at the ARRONAX cyclotron. The particles are irradiated using a He^{2+}-beam in the dose rate range of 0.8 – 4.4 kGy/min. The corrosion of UO_2 TRISO particles is investigated in view of grain boundary effects and secondary phase formation and the influence of hydrogen. The experiments started in 2013 with studies on the role of grain boundaries, followed by investigations of fuel particle corrosion under hydrogen and in varying dose rates.

Status and results

The oxygen diffusion studies at JRC-ITU were held back in 2013 by an autoclave failure which resulted for safety reasons in a complete replacement of the set-up located in the hot cells for spent fuel handling. Despite all efforts undertaken it was not possible to get the set-up back in working conditions because of the delivery time of special valves needed. It was decided to prolong WP2 from 33 to 36 months and to report all results obtained until month 33 in FIRST Nuclides. Later results will be published in an open journal with reference to FIRST Nuclides [13]. Instead diffusion profiles measured on UO_2 have been analysed and modelled. It was found that the diffusion of oxygen into the uranium oxide surface occurs in parallel processes and not layer by layer [2], [3], [18], [19], [20].

JÜLICH investigates UO_2TRISO coated particles from spent HTR fuel (burn-up ~100 GWd/t_{HM}). UO_2 fuel kernels were exposed to synthetic groundwater (19 mM NaCl and 1 mM $NaHCO_3$) for 276 days under oxic (air) and anoxic/reducing (Ar/H_2) conditions. The U concentration in the leachate was below detection limit, indicating extremely low matrix dissolution. Within the leaching period of 276 days ^{90}Sr and $^{134/137}Cs$ fractions located at grain boundaries were released and contributed to the IRF up to max. 0.2 % respectively 8 %. Depending on the environmental conditions, different release functions were observed. Second relevant release steps occurred in air after ~ 120 days, indicating the formation of new accessible leaching sites. ESEM (environmental scanning electron microscope) investigations were performed to study the impact of leaching on the microstructure. In oxic environment, numerous intragranular open pores acting as new accessible leaching sites were formed and white spherical spots containing Mo and Zr were identified. Under anoxic/reducing conditions numerous metallic precipitates (Mo, Tc and Ru) filling the intragranular pores and white spherical spots containing Mo and Zr, were detected [4], [5], [6], [14], [15], [16].

CNRS investigates the oxidation of UO_2 in unirradiated HTR fuel kernels by α-radiolysis products of water. Radiolysis products are produced by 66.5 MeV He^{2+} beam irradiation of water in the ARRONAX cyclotron giving a dose rate of 4.37 kGy/min. The UO_2 oxidation is studied by simultaneous characterisation of secondary phases on the UO_2 surface by Raman spectroscopy, quantification of the radiolysis products H_2O_2 in water (UV-VIS spectrophotometry) and H_2 in the gas phase (micro gas chromatography) and determination of U in solution by inductively coupled plasma mass spectrometry (ICP-MS).

The obtained results show that gaseous H_2 produced by water radiolysis completely inhibits the UO_2 corrosion by interaction between H_2 and the UO_2 surface. The UO_2 radiolytic corrosion expressed as a function of the absorbed dose show a ten-fold higher dissolution rate for the lower dose rate (0.8 kGy/min) than that found for the higher one (4.4 kGy/min). If OH radicals are produced near the UO_2 surface they interact directly with the UO_2 surface and not with each other to form H_2O_2. In this

case also the radiolytic corrosion is higher than in presence of molecular H_2O_2. It is also shown that the UO_2 radiolytic corrosion under He^{2+} radiation occurs essentially on the grain boundaries and not on the crystallized UO_2 grains [7], [8], [9], [10], [17].

Dissemination

Publications, reports, or contributions in reports, proceedings:

[1] Wegen, D.H. (2013). *Overview WP2: Gas Release + Rim and Grain Boundary Diffusion*. 2nd Annual Workshop Proceedings, 7th EC FP – FIRST-Nuclides, November 5th-7th, Antwerp, Belgium, KIT SCIENTIFIC Reports 7676, pp. 21-25.

[2] Carbol, P., Marchetti, I., Wegen, D.H. (2013). *WP2: Rim and grain boundary diffusion*. 2nd Annual Workshop Proceedings, 7th EC FP – FIRST-Nuclides, November 5th-7th, Antwerp, Belgium, KIT SCIENTIFIC Reports 7676, pp. 79-86.

[3] Carbol, P., Marchetti, I., Wegen, D.H., Bulgheroni, A., Wiss, T. (2014). *WP2: Grain boundary diffusion in spent fuel and poly-crystalline UO_2*. Final Annual Workshop, 7th EC FP – FIRST-Nuclides, 1st-2nd September, Karlsruhe, Germany.

[4] Curtius, H., Müller, E., Müskes, H.W., Klinkenberg, M., Bosbach, D. (2013). *Selection and Characterisation of HTR Fuel*.1st Annual Workshop Proceedings of the Collaborative Project "FAST/INSTANT release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-NUCLIDES), Budapest 09-11 October 2012, KIT SCIENTIFIC Reports 7639, pp. 41.

[5] Curtius, H., Müskes, H.W., Güngör, M., Liek, N., Bosbach, D. (2013). *First results on instant radionuclide release fraction from spent UO2 TRISO coated particles*. 2nd Annual Workshop Proceedings, 7th EC FP – FIRST-Nuclides, 5th-7th November, Antwerp, Belgium, KIT SCIENTIFIC Reports 7676, pp. 97-103.

[6] Curtius, H., Lieck, N., Kaiser, G., Güngör, M., Klinkenberg, M., Bosbach, D. (2014). *Instant radionuclide release fraction from spent UO_2TRISO coated particles and microstructure evolution*. Final Annual Workshop, 7th EC FP – FIRST-Nuclides, 1st-2nd September, Karlsruhe, Germany.

[7] Vandenborre, J., Traboulsi, A., Blain, G., Barbet, J., Fattahi, M. (2013). *Radiolytic Corrosion of Grain Boundaries onto the UO_2 TRISO Particle Surface*. 1st Annual Workshop Proceedings of the Collaborative Project "FAST/INSTANT release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-NUCLIDES), Budapest 09-11 October 2012, KIT SCIENTIFIC Reports 7639, pp. 161.

[8] Vandenborre, J., Traboulsi, A., Blain, G., Barbet, J., Fattahi, M. (2013). *Impact of Water Radiolysis on Uranium Dioxide Corrosion*. 2nd Annual Workshop Proceedings, 7th EC FP – FIRST-Nuclides, 5th-7th November, Antwerp, Belgium, KIT SCIENTIFIC Reports 7676, pp. 131-138.

[9] Traboulsi, A., Vandenborre, J., Blain, G., Humbert, B., Barbet, J., Fattahi, M. (2014). *Radiolytic Corrosion of Uranium Dioxide: Role of Molecular Species*, J. Phys. Chem. C, 118 (2), pp 1071–1080.

[10] Vandenborre, J., Traboulsi, A., Blain, G., Humbert, B., Haddad, F., Fattahi, M. (2014). *Radiolytic corrosion of uranium dioxide under He^{2+} irradiation*. Final Annual Workshop, 7th EC FP – FIRST-Nuclides, 1st-2nd September, Karlsruhe, Germany.

Presentations and poster:

[11] Wegen, D.H. (2013). *WP2: Gas Release & Rim and Grain Boundary Diffusion.* 2nd Annual Workshop, 7th EC FP – FIRST-Nuclides, 5th-7th November, Antwerp, Belgium.

[12] Wegen, D.H. (2014). *WP2 Summary: Gas Release & Rim and Grain Boundary Diffusion.* 3rd Annual Workshop, 7th EC FP – FIRST-Nuclides, September 1st-2nd, Karlsruhe, Germany.

[13] Carbol, P., Marchetti, I., Wegen, D.H. (2013). *Oxygen and water diffusion into 42 GWd/t_{HM} UO_2*. 2nd Annual Workshop, 7th EC FP – FIRST-Nuclides, November 5th-7th, Antwerp, Belgium.

[14] Curtius, H. (2013). *Instant radionuclide release fraction of high burn-up spent nuclear fuel*. 2nd Annual Workshop, 7th EC FP – FIRST-Nuclides, 5th-7th November, Antwerp, Belgium.

[15] Curtius, H. (2014). *Instant radionuclide release fraction from spent UO_2 TRISO coated particles and microstructure evolution*. Spent Fuel Workshop 2014, 3rd-5th September, Karlsruhe, Germany.

[16] Curtius, H. (2014). *Corrosion of spent fuels from research and prototype reactors under conditions relevant to geological disposal*. DAEF conference (Key topics in deep geological disposal), 24th-26th September, Köln, Germany.

[17] Traboulsi, A., Vandenborre, J., Blain, G., Barbet, J., Fattahi, M. (2013). *Impact of Water Radiolysis on Uranium dioxide corrosion*. Migration 2013, 8-13 September, Brighton, UK.

[18] Carbol, P., Bulgheroni, A., Wegen, D.H., Marchetti, I., Wiss, T. (2014). *Oxygen and water diffusion in UO_2 under oxidising and reducing conditions*. Final Annual Workshop, 7th EC FP – FIRST-Nuclides, 1st-2nd September, Karlsruhe, Germany.

[19] Bulgheroni, A. (2014). *Surface characterisation of oxidised UO_2 by SIMS*. Spent Fuel Workshop 2014, 3rd-5th September, Karlsruhe, Germany.

[20] Marchetti, I. (2014). *Surface species in UO_2 oxidative dissolution*. International workshop on surface reactivity and dissolution of spent nuclear fuel materials, Final Annual Workshop, 7th EC FP – REDUPP (Reducing uncertainty in performance prediction), 18–21 February, Stockholm, Sweden.

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Abstract: This report summarises the activities planned and performed in project months 25 - 33 by the beneficiaries collaborating in the component "*Rim and grain boundary diffusion*" of work package 2 (WP2) of the CP – FIRST-Nuclides project in 2014. The main achievements in the third project year are given.

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