Ph.D. defense

Institut de Chimie Séparative de Marcoule / CEA Marcoule
(UMR 5257, CEA, CNRS, Université Montpellier, ENSCM)

FLORENT TOCINO

will present his Ph.D. dissertation

Microstructural control of redox reactions at the solid/solution interface during the dissolution of uranium (IV) – based mixed oxides

The defense will take place on **Monday, December 14, 2015** at **2.00 pm**

in the Visiatome Auditorium

In the field of the use of actinides mixed oxides as potential fuels for the Gen(III) and Gen(IV) nuclear reactors, solid solutions with general formula $U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_{2-y}$, $U_{0.75}Nd_{0.25}O_{1.875}$, $U_{0.75}Gd_{0.25}O_{1.875}$ and $Th_{0.75}Nd_{0.25}O_{1.875}$ were prepared by thermal conversion of oxalate precursors. Dense pellets exhibiting various physico-chemical and microstructural properties (in terms of composition, homogeneity, densification rate, …) were prepared through sintering then submitted to dissolution tests. The multiparametric study of the dissolution, performed in nitric, sulfuric and hydrochloric media clearly underlined the important effect of the chemical composition on the chemical durability of the samples. Indeed, several parameters (including partial order related to proton activity, apparent activation energy) confirmed the significant modification of the preponderant dissolution mechanism for uranium-enriched samples. Moreover, the role of various nitrogen-based species was evidenced at the solid/solution interface. The evolving of solid/solution interfaces (reactive surface area, composition) during dissolution was monitored by the means of operando ESEM experiments. Preferential dissolution zones (triple junctions, grain boundaries, inter- and intra-granular porosities) were clearly observed for uranium-depleted samples. They induce a significant increase of the reactive surface area even for short progress of the reaction. On the contrary, the dissolution appeared more homogenous for uranium-enriched samples due to the existence of a preponderant mechanism associated to the oxidation of the uranium(IV) at the interface.

Keywords: Dissolution; Oxides; Redox; Interfaces; Microstructure