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Abstract

In this work, the oxidation of UO_2 by the radiolysis products of water at the solid/solution interface is investigated in function of the dose under open and close atmospheres. Irradiation is realized by He^{2+} beam provided by the ARRONAX cyclotron with an energy of 66.5 MeV and a dose rate of 4.37 kGy/min. The aim of this investigation is to determine the effect of the atmosphere (presence of H_2) and the dose on the UO_2 oxidation in order to couple for the first time (1) characterization of the secondary oxidized phases, (2) quantification of H_2O_2 and H_2 produced by water radiolysis and (3) determination of the quantity of uranium released into the solution. The kinetic of the solid surface oxidation is followed by Raman spectroscopy. H_2O_2 and H_2 are measured respectively by UV-VIS spectrophotometry and micro Gas Chromatography (μ-GC). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used to quantify the soluble uranium species released into the solution. Our results show that He^{2+} irradiation of water induced oxidation of the UO_2 surface which depended on the atmosphere and the dose rate. We present below the results obtained for two samples irradiated at a dose of 8.73 kGy under the two atmospheres mentioned above. Results shows the Raman spectra of unirradiated UO_2 (a) and a sample irradiated under open atmosphere (b, c, d). The spectra of the irradiated sample are obtained 0.3, 42 and 169 hours after contact with the irradiated water. When comparing the two spectra, 2 identical Raman signals can be observed at 445 and 560 cm^{-1}. The first one characterizes the U-O stretch in the fluorite structure of UO_2 and the second one indicates the presence of defects in the matrix. After irradiation, two Raman signals appear at 820 and 865 cm^{-1}. These vibration bands indicate the presence of studtite (UO_4 4(H_2O)) formed by oxidation of the UO_2 surface by H_2O_2 produced by water radiolysis. We have verified that studtite is not formed by oxidation of the UO_2 surface by O_2 present in the atmosphere. For the irradiated sample, $G(H_2O_2)$ formed by water radiolysis is 0.06 μmol/J and the quantity of uranium species released in the irradiated solution is 11.5 10^{-7} mol/L. For the sample irradiated under close atmosphere, oxidation is much slower due to the inhibition effect of H_2 produced by water radiolysis. In these conditions, $G(H_2O_2)$ and $G(H_2)$ are respectively 0.1 and 0.02 μmol/J. The concentration of Uranium species in the solution is 5.3 10^{-7} mol/L which is comparable to that published in the literature.
$G(H_2O_2)$ obtained in open atmosphere is two fold lower than that obtained in close one. In this last condition, H_2O_2 yield is equal to that of ultra-pure water which means that this molecule was not consumed. Moreover, $G(H_2)$ obtained in this work is lower than that obtained by radiolysis of ultra-pure water in similar conditions. From this, we can conclude

that H_2 has an inhibition effect on the UO_2 oxidation and this inhibition does not take place by direct effect on H_2O_2 but by interaction between H_2 and the UO_2 surface.

Introduction

This paper deals with the radiolytic corrosion at the UO_2 surface. We study the impact of water radiolysis onto the corrosion of the grain boundaries (GB) present at the TRISO particle surface. The influence of H_2 produced by water radiolysis on the UO_2 corrosion is also studied. More details on the context of this study is published elsewhere (Kienzler et al., 2012). The aim of this work was to investigate experimentally the effect of molecular radiolytic species (H_2 and H_2O_2) produced by localized $^4He^{2+}$ radiolysis of water on UO_2 corrosion in function of different parameters. Water in contact with UO_2 particles was then irradiated by $^4He^{2+}$ beam at different absorbed doses and under different atmospheres in order to evaluate the effect of H_2 and the absorbed dose on the corrosion process. To fulfill this work, we chose to investigate the corrosion of the surface of solid particles by Raman Spectroscopy which is known to be very efficient in surface characterization of solid state materials. Soluble uranium species leached into the solution were analyzed by Inducted Coupled Plasma Mass Spectrometry (ICP-MS) technique. H_2O_2 and H_2 produced by water radiolysis were respectively quantified by UV-VIS Spectrophotometry and Gas Chromatography (μ-GC) in order to calculate their radiolytic yields, compare them to those of pure water and clarify the role of these two species in the UO_2 corrosion.

Material and Methods :

The experimental section (analytical tools and irradiation conditions) is described elsewhere (Kienzler et al., 2012). 3 irradiations were performed for 3 sets of sample: (1) irradiation under open to air atmosphere (oxidative conditions without H_2), (2) close with air atmosphere (oxidative conditions with H_2 produced by water radiolysis), and (3) close with Ar/H_2 (4%) atmosphere (reductive atmosphere where H_2 is initially added into the system before irradiation by the Ar/H_2 (4%) gas).

Results

1.UO_2 Surface Characterization

UO_2 TRISO particle is constituted of a UO_2 based kernel (500 µm of diameter) composed by grains and grain boundaries (**Figure** 1). The grain size has been measured between 10 and 20 µm. After irradiation, SEM pictures were realized on the surface particles in order to determine the zones most affected by the corrosion process (**Figure** 2). **Figure** 2 clearly shows that regardless the irradiation atmosphere, the grain boundaries are a lot more degraded than the UO_2 grains. It appears too that the corrosion did not occur homogeneously on the entire surface. Some regions of the grains surface are indeed more corroded. The corrosion can be considered as localized to the GB.
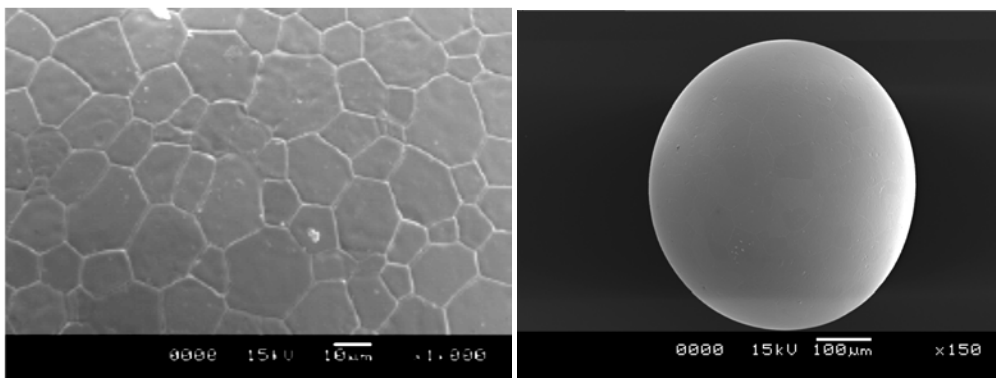
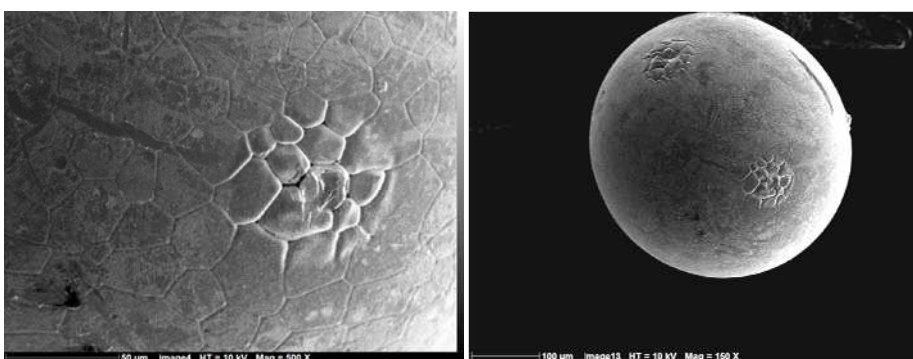**Figure 1** : SEM picture of the surface of an unirradiated UO_2 particle.

Figure 2 : SEM pictures of the surface of a UO_2 particle corroded in open to air atmosphere.

The spectrum of the unirradiated UO_2 is presented in **Figure** 3. It presents two characteristic bands around 445 cm^{-1} and 560 cm^{-1}. The former is affected to the triply degenerated Raman active mode (T_{2g}) of U-O stretch (Amme et al., 2002; Amme et al., 2005; Desgranges et al., 2012; He and Shoesmith, 2010; Manara and Renker, 2003) whereas the latter characterizes defects present initially in the UO_2 fluorite structure (He and Shoesmith, 2010).

To estimate the Raman spectral modifications brought by the radiolytic products of water in the different studied atmospheres, a comparison was made between the UO_2 spectra before and after irradiation. The results showed that after irradiation in close atmospheres, the spectra of the UO_2 particles remained stable in function of the dose (not presented in this paper). When water in contact with the UO_2 particles was irradiated in open to air atmosphere, no spectral modifications were observed until 21.8 kGy deposited in the solution. From 43.7 kGy, modifications can be seen between 800 and 900 cm^{-1} and appear clearly at the dose of 87.3 kGy. Two peeks appear indeed at 825 and 860 cm^{-1}. They characterize the metastudtite ($UO_2(O_2)$ $2H_2O$) (Amme et al., 2002; Canizarès et al., 2012; Guimbretière et al., 2011) formed on the UO_2 surface by oxidation with H_2O_2 produced by water radiolysis according to the reaction (**i**) (Corbel et al., 2006) :

$$UO_2 \; + \; 2H_2O_2 \; \rightarrow \; UO_2(O_2) \, (H_2O)_2 \hspace{3cm} \textbf{(i)}$$

After irradiation, temporal evolution of the solid particles was followed by Raman spectroscopy. The results showed that Raman spectra of the samples irradiated with an irradiation time t = 1 min remained unchanged after two months of the experiment. It seems that in these conditions, the concentration of H_2O_2 produced by water radiolysis was not sufficient to oxidize the UO_2 surface. For t ≥ 3 min, Raman spectra of the irradiated particles evolved slightly in function of time until one week after irradiation and then remained stable.
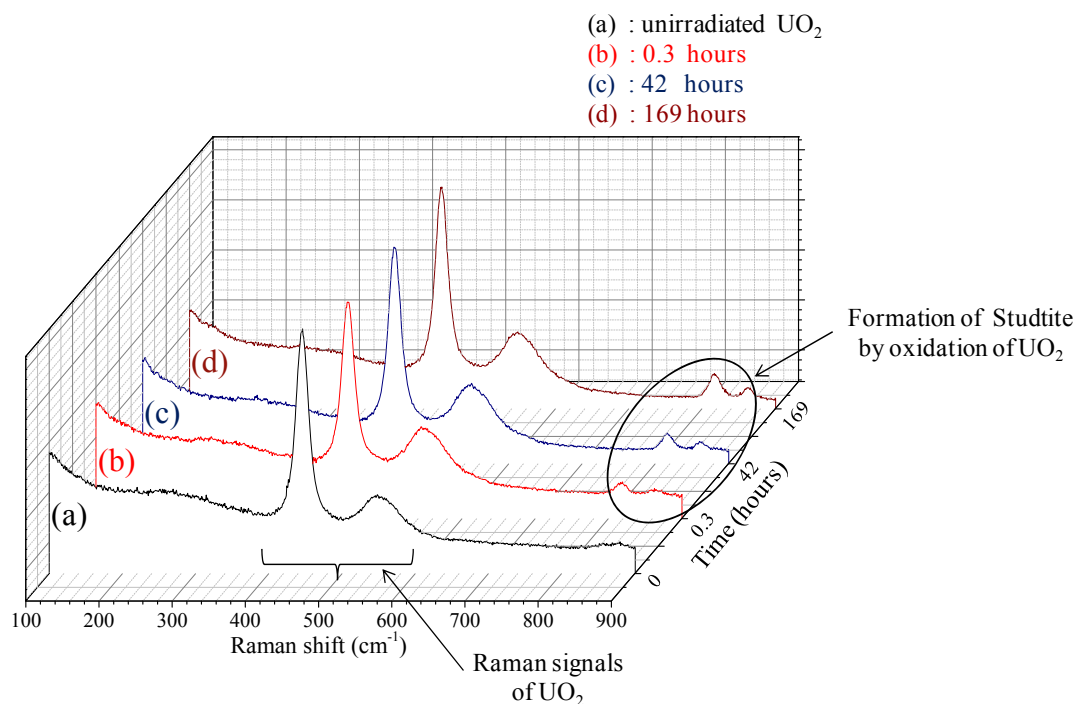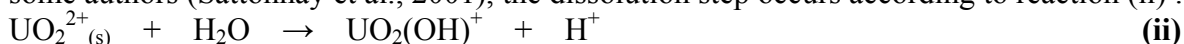
(a) : unirradiated UO$_2$
(b) : 0.3 hours
(c) : 42 hours
(d) : 169 hours

Figure 3 : Raman spectra of unirradiated UO$_2$ ((a)) and a sample irradiated at 8.73 kGy under open atmosphere ((b), (c) and (d)). The spectra (b), (c) and (d) are obtained 0.3, 42 and 169 hours after contact with the irradiated solution.

2.Uranium Solubility and Dissolution Rate

After irradiation, water in contact with the UO$_2$ particles was collected to quantify the soluble uranium species leached into the solution. Indeed, the metastudtite phase formed on the UO$_2$ surface after oxidation by H$_2$O$_2$ produced by water radiolysis underwent later a dissolution step where uranyl ions (UO$_2^{2+}$) were leached into the solution. The mechanism of this dissolution reaction in ultra-pure water was rarely discussed in the literature. According to some authors (Sattonnay et al., 2001), the dissolution step occurs according to reaction (ii) :

$$UO_2{}^{2+}{}_{(s)} \quad + \quad H_2O \quad \rightarrow \quad UO_2(OH)^+ \quad + \quad H^+ \tag{ii}$$

However, (Sattonnay et al., 2001) proposed this dissolution mechanism based on a pH decreasing observed in their case after the solution irradiation. But, in our work measurement of the irradiated solutions acidity after each irradiation showed that pH did not evolve significantly and remained between 6.5 and 7.5. This means that the above proposed mechanism (reaction (**ii**)) does not occur in our case.

We have followed the variation of the soluble uranium species concentration leached into the solution after irradiation in function of the dose and the irradiation time in both open and close atmospheres. Regardless the irradiation atmosphere, the quantity of soluble uranium species increased with the dose and then remained constant from 43.6 kGy. At this latter dose, concentration of soluble uranium species found in close with air atmosphere (5.25 10^{-7} mol l^{-1}) is two-fold lower than that observed in open to air atmosphere (11.49 10^{-7} mol l^{-1}) due to inhibition of UO$_2$ oxidation by H$_2$ produced by water radiolysis. Values of [U] measured in our system at the steady state are presented in **Table** 1 for an irradiation time of 10 min together with the normalized leaching rate (r). Moreover, **Table** 1 presents also UO$_2$ dissolution rate values obtained from literature in order to compare it to our data. When UO$_2$ particles were irradiated between 10 and 20 min in close with air atmosphere, concentration of Uranium species remained practically constant. The obtained values were respectively 4.44 ± 0.5 and 5.25 ± 0.5 10^{-7} mol l^{-1} for the latter mentioned irradiation time. These values are

comparable to most solubility data reported in the literature (Casas et al., 2009; Grambow et al., 2004; Jégou et al., 2003; Shoesmith and Sunder, 1992). However, we believe that in our work the thermodynamic equilibrium of the UO_2 particles dissolution was not achieved due to their composition of grains and grain boundaries. In these conditions, the dissolution rate was equal to 13.5 g m^{-2} d^{-1}. A comparison of our dissolution rates with literature data is given in **Table** 1. Despite the similarity with [U] reported in the literature, r values obtained in this investigation are at least 10^3 fold higher. It seems then that with the irradiation conditions used in our work, the UO_2 oxidation/dissolution mechanism occurred with a faster kinetic. This is very probably due to the impact of the high doses deposited into the irradiated solution for this work. In order to apprehend the dose impact on the UO_2 corrosion, we propose here a new methodology to express the dissolution rate. This methodology consists in calculating the dissolution rate in function of the dose deposited into the solution and not in function of the irradiation time. Thus, the new dissolution rate r' can be defined as follow :

$$r' = \frac{V}{S} \frac{d[U]}{dd} M_{UO_2}$$

Where $d[U]/dd$ (mol m^{-3}) is the variation of soluble uranium species in function of the dose deposited into the solution. In our case the r' values are 2.01 µg m^{-2} Gy^{-1} for the open with air atmosphere experiment and 1.11 µg m^{-2} Gy^{-1} for the close with air atmosphere one. These results confirm that the reducing atmosphere (in presence of H_2) has a strong diminishing impact onto the UO_2 dissolution rate. Moreover, we have recalculated the same new dissolution rate r' from literature data (Grambow et al., 2004; Jégou et al., 2003) (**Table** 1) in order to compare it to our results. Even after taking into account the effect of the dose, r' values obtained in this investigation still higher (**table** 1). However, the dose rate used in our work is very high. It appears then that the dose rate is the main parameter which controls the UO_2 dissolution rate under irradiation.

Table 1 : Steady state U concentrations, Dissolution rates (r and r') of UO_2 and experimental conditions used in this study and others found in the literature.

Ref.	Physical aspect UO_2	$^4He^{2+}$ Beam	Dose Rate Gy min^{-1}	Atm.	[U] 10^{-7} mol l^{-1}	Diss. rate r mg m^{-2} d^{-1}	Diss. rate r' µg m^{-2} Gy^{-1}
This work	Particle	External source*	4366	Ox	11.49	13500	2.01
				Red	5.25	7000	1.11
(Shoesmith and Sunder, 1992)	Pellet	Internal	No	Ox		0.5	X
(Casas et al., 2009)	Particle	No	0	Red		23.3	X
(Grambow et al., 2004)	Colloid	External source*	52.7	Red		15.7	0.246
(Jégou et al., 2003)	Pellet	Internal**	18	Ox		2.5	0.095
			1.8	Ox		0.2	0.076

* $^4He^{2+}$ Beam produced by cyclotron facility
** Doped UO_2 with Pu

3.H_2 and H_2O_2 Chemical Yields
When the UO_2 particles were irradiated in close with air atmosphere, H_2 produced by water radiolysis was quantified by calculating its radiolytic yield (G) in order to compare it to that of pure water and explain any gas consumption due to the inhibition of the UO_2 corrosion

process. In our work, the solution used during irradiation is ultra-pure water (ρ = 1 kg l^{-1}) and the mean G(H$_2$) was 0.02 ± 0.002 µmol J^{-1}. It corresponds to the slope of the curve representing the variation of H$_2$ concentration in function of the dose. (Crumière et al., 2013) irradiated ultra-pure water by a cyclotron ^{4}He^{2+} beam with a 64.7 MeV energy and doses up to 800 Gy in Argon saturated atmosphere. G(H$_2$) obtained in their work was 0.061 ± 0.006 µmol J^{-1} which is three-fold higher than that found in this investigation (G(H$_2$) = 0.02 ± 0.002 µmol J^{-1}). The irradiation conditions used by (Crumière et al., 2013) are very similar to those used in our work which means that for the system UO$_2$/ultra-pure water, a non negligible part (around 2/3) of the H$_2$ produced by water radiolysis was consumed certainly by inhibition of the UO$_2$ oxidation process.

In both open to air and close with air atmospheres, concentrations of H$_2$O$_2$ produced by water radiolysis was determined by the Ghormley method (Ghormley and Hochanadel, 1954) to analyze the effect of the irradiation atmosphere on its consumption by the UO$_2$ oxidation process. During this study, we have followed the variation of H$_2$O$_2$ concentration produced by water radiolysis under open to air and close with air atmospheres in function of the dose. It shows that concentration of H$_2$O$_2$ produced by water radiolysis increased with the dose and then reached a steady state from 21.8 kGy and 65.5 kGy in open to air and close with air atmospheres respectively. At these latter doses, [H$_2$O$_2$] values were respectively 1.4 10^{-4} and 5.5 10^{-4} mol l^{-1} which means that H$_2$O$_2$ concentration was four-fold higher when the UO$_2$ particles were irradiated in presence of H$_2$. It seems then that in the latter conditions consumption of H$_2$O$_2$ and thus oxidation of the UO$_2$ surface was mainly inhibited by H$_2$ produced by water radiolysis. Radiolytic yields of H$_2$O$_2$ were also calculated and the values obtained were 0.06 ± 0.006 and 0.1 ± 0.01 µmol J^{-1} in open to air and close with air atmospheres respectively. G(H$_2$O$_2$) obtained in open to air atmosphere is two fold lower than that obtained in close with air one. In this last condition, H$_2$O$_2$ yield is equal to that of ultra-pure water (LaVerne, 2004; Pastina and LaVerne, 1999; Yamashita et al., 2008a; Yamashita et al., 2008b) which means that this molecule was not consumed whereas a non-negligible part of H$_2$ was consumed. From this, we can conclude that in open to air atmosphere, half of the H$_2$O$_2$ produced by water radiolysis was consumed by oxidation of the UO$_2$ surface leading to the formation of metastudtite secondary phase. We can conclude too that H$_2$ has an inhibition effect on the UO$_2$ oxidation and this inhibition does not take place by direct effect on H$_2$O$_2$ but by interaction between H$_2$ and the UO$_2$ surface.

Conclusions and Future work

In conclusion, this work brings some light on the radiolytic corrosion of UO$_2$ by identification of (1) the oxidized secondary phase formed (metastudtite) and following its temporal evolution, (2) the H$_2$ role as an inhibitor agent, (3) the oxidative role of H$_2$O$_2$ and (4) the quantity of U species released. Detailed mechanisms of UO$_2$ corrosion/oxidation will be proposed taking into account the phenomena of water radiolysis.

Furthers studies will be performed in order to determine the role of the radical speces produced by water radiolysis on UO$_2$ corrosion. Moreover, spacial resolution technique will be used in future surface characterization experiments in order to localize the corrosion on the grain boundaries as shown with SEM pictures.

Acknowledgement

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