

Fuel Pellets Phase Composition Evolution During Steam or Air Oxidation

IULIA DUMITRESCU^{1*}, MARIA MIHALACHE¹, ALICE DINU¹, TIBERIU MELEG¹, DUMITRU OHAI², MARIOARA ABRUDEANU²

¹Institute for Nuclear Research, 1 Campului Str., 115400, Pitesti, Romania

²University of Pitesti, 1 Targul din Vale Str., 110040, Pitesti, Romania

In this paper the results of laboratory tests on oxidation behavior of non-irradiated UO₂ fuel pellets in a SETARAM Thermoanalyzer, in steam and air atmosphere are presented. Isothermal oxidation has been obtained performed in air-steam mixture with contents of 0 and 95% in the temperature range 400 ÷ 1200°C. The samples were investigated by scanning electron microscopy, X-ray diffraction and laser diffraction. The results show differences in chemical composition, particles size distribution and morphology depending on temperature and steam content of the atmosphere. In air, for temperatures below 700°C a mixture of uranium oxides compounds is formed while for temperatures above 700°C only U₃O₈ oxide is formed. Experiments in humid atmosphere revealed the formation of an additional compound -U₃O₈(OH)₂ for all temperatures domain.

Keywords: nuclear fuel, oxidation, severe accidents, UO₂ fuel pellets

Studies of the physico-chemical phenomena concerning severe accidents in nuclear power stations are very challenging since in this area is not possible to conduct experiments on a real-world scale and only laboratory tests can be used. This type of tests permits each phenomenon to be considered separately [1-5].

The oxidation reactions that may occur on the zircaloy claddings and on fuel pellets in case of a severe nuclear accident lead to a decrease in the fuel mechanical stability and to an increase in fission products volatility [6-9].

Also, in order to define proper conditions for secure storage of spent fuel it is important to understand the oxidation behaviour of UO₂ fuel pellets at low temperatures [10-14].

The aim of this paper is to obtain experimental data necessary to the modelling of fuel pellets behaviour in the case of a severe nuclear accident in CANDU reactors.

The paper describes the oxidation tests of UO₂ fuel pellets in a SETSYS Evolution SETARAM Thermoanalyzer in air and steam atmosphere in the temperature range 400-1200°C.

Experimental part

Two sets of oxidation experiments of UO₂ pellets in 0% and 95% steam in air atmosphere were performed in a SETARAM SETSYS Evolution Thermoanalyser. The temperature range was 400 ÷ 1200°C. The time duration of experiments was 4 h, except the D6 experiment where the duration was 2.5 h. The oxidation tests conditions are presented in table 1. The gas flow rate used in tests was 50 mLmin⁻¹.

The samples were non-irradiated UO₂ sintered fuel pellets, manufactured by pressing and then sintering the green pellets for 4h at 1700°C in a Degussa VSL 10/18 furnace using natural UO₂ powder. The diameter of pellets was approximately 3mm with 2 ÷ 2.5mm thickness, to fit to the 100 µL thermo analyzer crucible. The mass of each fuel pellets was about 0.2g UO₂.

The samples were weighed and placed in an Al₂O₃ crucible. Then the crucible was introduced in the SetSYS Evolution Thermoanalyzer furnace. The samples were

Table 1
TEST SAMPLES AND THEIR OXIDATION CONDITIONS

SAMPLE ID	Temperature (°C)	Steam in Air (%)	Time (h)
A1	400	0	4
D1	400	95	4
A2	500	0	4
D2	500	95	4
A3	600	0	4
D3	600	95	4
A4	700	0	4
D4	700	95	4
A5	800	0	4
D5	800	95	4
A6	900	0	4
D6	900	95	2.5
A7	1000	0	4
D7	1000	95	4
A8	1100	0	4
D8	1100	95	4
A9	1200	0	4
D9	1200	95	4

heated up to working temperature in an inert atmosphere (argon).

During the tests various data (temperature, gas flow rate and atmosphere composition) were recorded continuously. The weight change of samples was measured and the TG curves were obtained. The humid atmosphere was created with the WETSYS controlled humidity generator.

The samples were dimensionally, morphologically and cristallografically investigated after oxidation using the Horiba Particle Size Analyser, the TESCAN VEGA LMU scanning electron microscope and the X'Pert Pro MPD_PanAnalytical diffractometer, respectively.

Results and discussions

To study the temperature effect on oxidation the samples were exposed in air-steam mixture with a steam content of 0% and 95% at temperature in the range 400 ÷ 1200°C.

The effect of steam content in air on UO₂ samples oxidation is illustrated in figure 1 which presents the mass variation during isothermal oxidation kinetics at 500°C (fig.1a), 800°C (fig.1b) and 1000°C (fig.1c). At 500°C it can

* email: iulia.dumitrescu@nuclear.ro

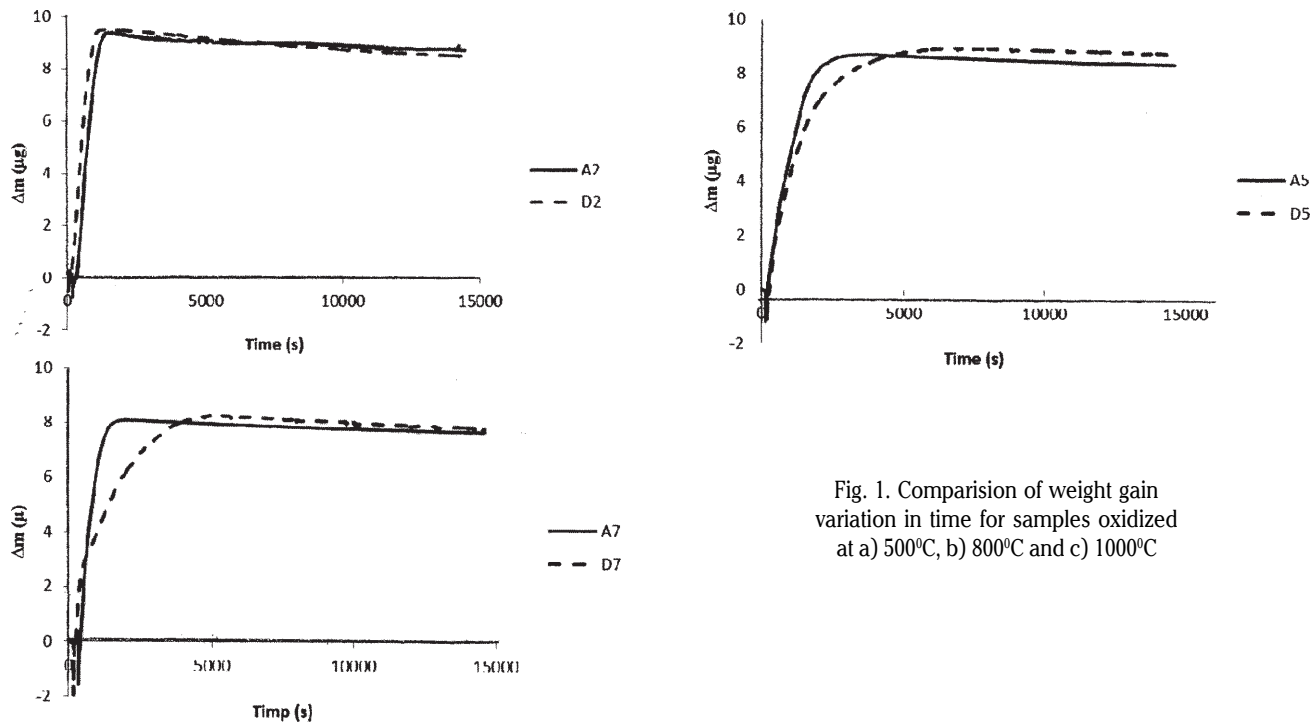


Fig. 1. Comparison of weight gain variation in time for samples oxidized at a) 500°C, b) 800°C and c) 1000°C

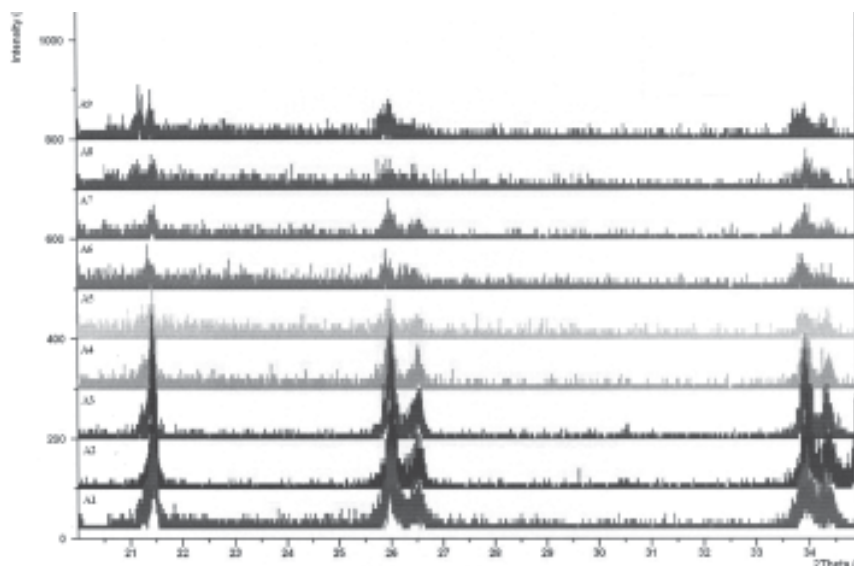


Fig. 2. X-Ray diffraction patterns for samples oxidized in air and temperatures between 400÷1200°C

Table 2

VALUES OF OXIDES CONTENT IN THE FINAL POWDER FOR SAMPLES OXIDIZED IN AIR OR STEAM ATMOSPHERE

SAMPLE ID	OXIDES CONTENT IN THE FINAL POWDER (%)		
	U ₃ O ₈	UO ₃	U ₃ O ₈ (OH) ₂
A1	58	42	-
A2	64	36	-
A3	71	29	-
A4	89	11	-
D1	29	-	63
D2	25	-	65
D3	26	-	63
D4	96	-	4
D6	63	-	37
D7	66	-	34
D9	55	-	45

be seen that the both curves are similar no matter the steam content, while at higher temperatures (800 and 1000°C) the mass increase rate is more rapid in the case of air oxidation (A5 and A7 samples). However, after reaching the limit, the mass increase is higher during oxidation in steam atmosphere (D5 and D7 samples).

The X-ray diffraction spectra obtained for samples exposed in air at different temperatures (A1÷A9) are presented in figure 2 and they reveal the formation of a mixture of two oxide compounds (UO₃ and U₃O₈) at 400-

700°C while for temperature above 800°C only U₃O₈ appears. The evolution of the compounds ratio with temperature is presented in table 2, for temperature range of 400÷700°C; this table illustrates the increasing of U₃O₈/UO₃ ratio with temperature. The U₃O₈ content in samples is increasing from 58% at 400°C to 89% at 700°C. Increasing the temperature from 800°C the samples are completely transformed in U₃O₈.

For samples exposed in a steam-air mixture (95% steam in air) the X-ray diffraction spectra are presented in figure 3 and show the formation of a mixture with three compounds: UO₃, U₃O₈ and U₃O₈(OH)₂ for temperatures between 400 and 600°C. However for 700÷1000°C range only two compounds -U₃O₈ and U₃O₈(OH)₂-are formed. The ratio between the 3 compounds is almost the same in the case of steam-air exposure in the temperatures domain from 400 to 600°C as it can be seen in table 2. The content of U₃O₈(OH)₂ is around 64%, while U₃O₈ and UO₃ contents are about 27 and 9%, respectively.

At higher temperatures (700÷1200°C) the U₃O₈/U₃O₈(OH)₂ ratio decreases with temperature. In this case the uranium trioxide formed by oxidation is gradually transformed in uranium oxide hydroxide. The content in

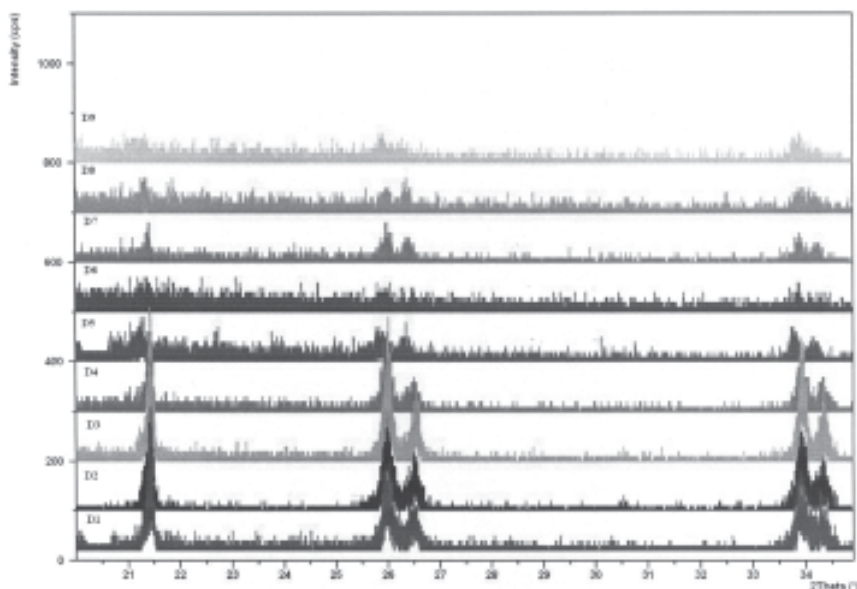


Fig. 3. X-Ray diffraction patterns for samples oxidized in (95%steam in air) atmosphere for temperatures between 400÷1200°C

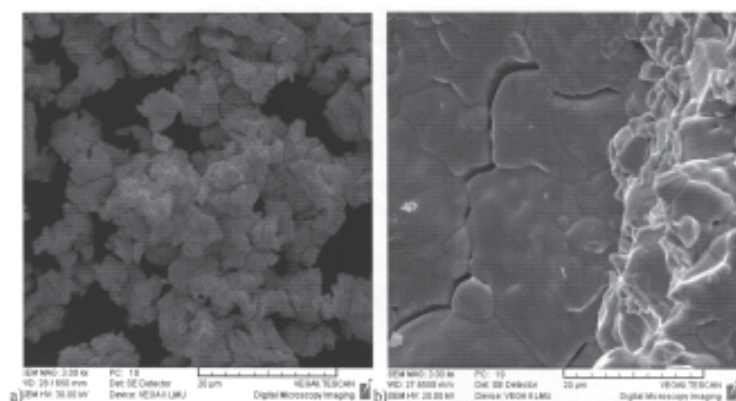


Fig. 4. SEM micrographs of samples a) A1 and b) A7

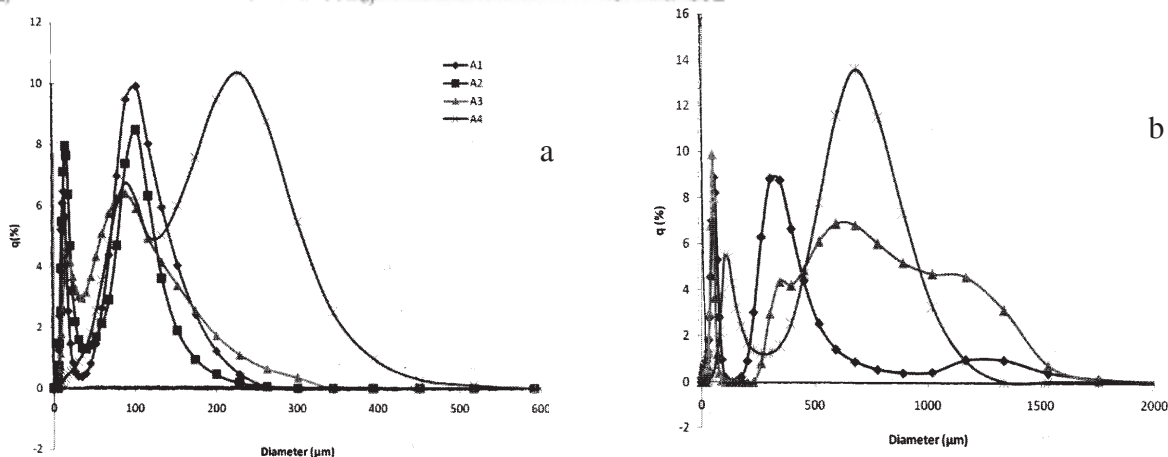


Fig. 5. Particles size distribution of samples treated in air: a) between 400-700°C (A1, A2, A3, and A4) b) 800- 1200°C (A5, A7, A9)

$U_3O_8(OH)_2$, enhances from 4% at 700°C to 45% at 1200°C (table 2). The intermediary oxide compound UO_3 has not been observed at these temperatures.

Unlike air oxidation of UO_2 , where for temperatures above 800°C only U_3O_8 was formed, for air-95%steam atmosphere even at temperatures around 1200°C two compounds were formed, namely U_3O_8 and $U_3O_8(OH)_2$.

Morphological aspects of samples exposed in air are presented in figure 4 and reveal the formation of a fine powder (fig.4a) while after exposure at 1000°C the sample presents secondary grains inside the initial grains and the fragmentation of samples in large compacts (fig.4b). A possible explanation may be the beginning of the recrystallization process due to temperature increase. This is also demonstrated by the particle size distributions analysis presented in figure 5. For samples A1 ÷ A4, exposed in air, the maximum particle diameter of around 500 µm while for samples A5 ÷ A9 the maximum particle diameter

is around 1500 µm. However, in both cases, the formation of two particles classes has been observed. For temperatures in the range from 400 to 700°C a fine fraction with average particle size diameter of about 10µm and a fraction with a particle size diameter of about 100µm appeared.

The average particle size diameter of the fine fraction in the case of higher temperatures (800-1200°C) is around 100µm and the average particle size diameter of the second fraction is about 700µm (fig.5b). The increase of particle size diameter with temperature enhance can be observed.

The SEM images of samples after exposure in (95%steam in air) atmosphere are presented in figure 6 and display intra and intergranular cracks for 500°C oxidation (D2) and rounded and linked particles for D7 sample treated at 1000°C.

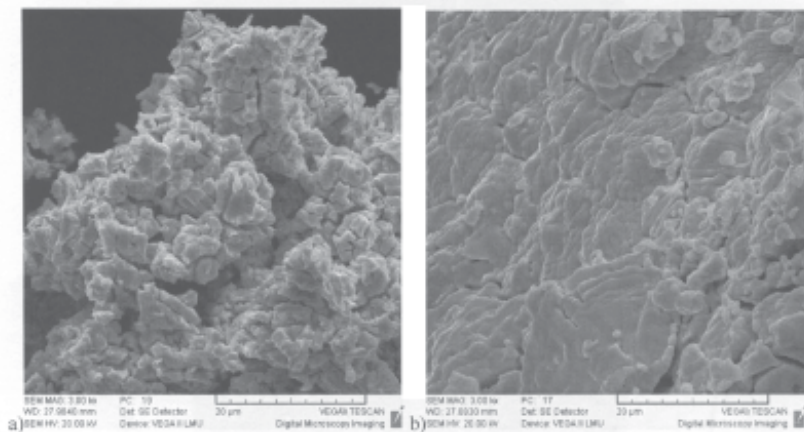


Fig. 6. SEM micrographs of sample oxidized in (air- 95% steam) atmosphere: a) D2, b) D7

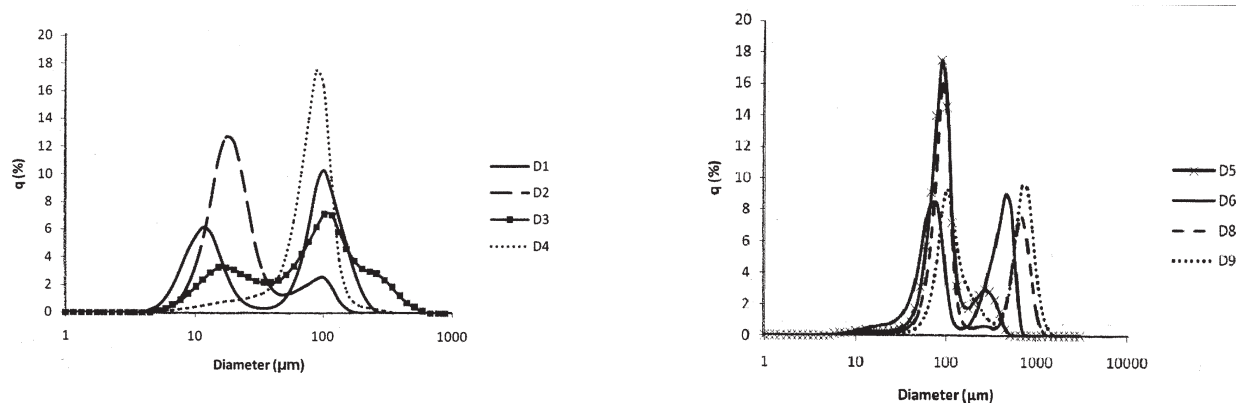


Fig.. 7. Particles size distribution of samples treated in humid atmosphere: a) between 400-700°C (D1, D2, D3 and D4) b) 800- 1200°C (D5, D6, D8 and D9)

A bimodal distribution of the fragments for all temperatures and a tendency of increasing the content of large particles with temperature have been observed for the samples exposed in (95%steam in air) atmosphere (fig.7). Also, two temperature domains with different behaviour of samples were observed like in the case of air oxidation. For temperature from 400 to 600°C the average particle size of the fine fraction was about 10μm and the second fraction had particles with an average diameter of about 100μm. For temperatures above 700°C the fine fraction presented an average particle size of about 100μm and the second fraction had the average diameter of about 600μm.

Conclusions

We have shown in the present work that the isothermal oxidation performed in air-steam mixture at temperatures between 400°C and 1200°C depends on test temperature and atmosphere composition.

During air oxidation at 400÷700°C uranium dioxide pellets convert into a mixture of UO_3 and U_3O_8 oxide compounds, while for temperatures between 800 and 1200°C only uranium trioxide U_3O_8 is formed. The U_3O_8 content of samples increases with temperature from 58% at 400°C to 100% at 700°C.

In a humid atmosphere the intermediary UO_3 compound is formed until 600°C and for all tested temperatures, in parallel with the most stable oxidation product (U_3O_8), the $U_3O_8(OH)_2$ compound is formed.

Morphological aspects of samples reveal the formation of a fine powder at lower temperatures and the beginning of the recrystallization process at temperatures above 1000°C with bigger compact grains formation.

The particle size distributions of samples after oxidation show a bimodal distribution of the powders for all

temperatures. A tendency of increasing the U_3O_8 content of large particles with temperatures can be shown.

Acknowledgements: This work was partly funded by EU under the FP7-SARNET 2 Project and by Institute for Nuclear Research-Pitesti.

References

- ***Research and development with regard to severe accidents in pressurized water reactors- Repport CEA-2007/351- p.6
- SONG, K., KIM, Y., KIM, B., LEE, J., KIM, H. S., YANG, M. S. and PARK, H.S., J. Korean Nucl. Soc., **28** (4), , 1996, p.366
- *** Analysis of Severe Accidents in Pressurized Heavy Water Reactors, IAEA-TECDOC-1594, IAEA, Vienna, 2008, p. 28
- GRIMES, R.W., CATLOW, C.R.A., Phil. Trans. R. Soc. Lond. A, **335**, 1991, p.609
- KUDO T., KIDA, M., NAKAMURA, T., NAGASE., F. and FUKETA, T., J. NUCL.SCI. and TECH., **44** (11), 2007, p.1428
- VALDIVIESO, F., FRANCON, V., BYASSON, F., PIJOLAT, M., FEUGIER, A., PERES, V., J.Nucl. Mat., **354**, 2006, p.85
- POPA, L., RADULESCU, M., DINU, A., VELCIU, L., BRANZOI, I., Rev. Chim. (Bucharest), **59**, no.2, 2008, p.140
- TAYLOR, P., J.Nucl.Mat., **344**, 2005, p.206
- KEON, S.K., YOU, G.S., MIN, D.K., RO, S.G. and KIM, E.K., J. Korean Nucl. Soc., **29**, 1997, p.93
- THOMAS, L. E., EINZINGER, R. E. and WOODLEY, R. E., J. Nucl. Mater, **166**, Nr. 310, 1989, p. 243
- MCCRACKEN, D.R.,- AECL **8632**- 1985, p.1
- THOMAS, L. E., SLAGLE, O., and EINZINGER, D., J. Nucl. Mater. **184**, 1991, p.117
- LIVOLANT, M., PORACCHIA, A., Core degradation in pressurized water reactor during severe accidents, Procc. of SMIRT 12, 1993, p.115
- HOFMANN, P., HAGEN, S., SCHANZ, G., SKOKAN, A., Chemical Interactions of Reactor Core Materials Up to Very High Temperatures, Kernforschungszentrum, Karlsruhe, Jan.1989

Manuscript received: 20.03.2014