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New measurements on $(U,Pu)O_2$ properties within european projects : ESNII+ and ESFR-SMART.

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Abstract – *A set of oxide fuel properties is needed to develop the fast neutron systems and to design prototypes of the Sodium Fast Reactor, the Gas-cooled Fast Reactor and a heavy liquid metal cooled Accelerator Driven System. The ESNII+ project (2014-2017) and then ESFR-SMART project (2017-2022) have a work package dedicated to this item : providing thermal and mechanical properties of MOX fuel through a catalog and performing complementary measurements on specific properties. The data and models available in the literature for each property were reviewed and experimental workplan was proposed for the European projects mentioned. Property measurements are done on existing fresh and irradiated fuel samples, identified to cover the fuel characteristics in term of plutonium content, density, stoichiometry, temperature and burn-up. Measurements have been performed and are continuing on thermal diffusivity, heat capacity, melting temperature, thermal expansion and Young modulus. The paper presents the results obtained on properties measurements and the comparison with existing and available data.*

I –INTRODUCTION

The ESNII+ project with its workpackage *7-FUEL SAFETY* and then the ESFR-SMART project with its workpackage *2.5-FUEL SAFETY* aim to provide an updated European catalog of the $(U,Pu)O_2$ fuel properties needed for the fuel element design of the ESNII prototype reactors.

The thermal and mechanical properties of the fuel yield the dominant contribution to the uncertainties in safety behavior evaluations (margin to melt for the fuel and the risk of clad failure), in nominal conditions as well as during transients.

Compared to LWR UO_2 and MOX fuels, much less data is available for FBR fuels, in particular recent data and data obtained for irradiated fuels.

The improvement of fuel properties is achieved by new measurements for fresh and irradiated fuels. The accuracy is rigorously assessed and correlations with burn-up are proposed. These property measurements are done on existing fresh and irradiated fuel samples, identified to cover the characteristics (linear power, Pu content, burn-up range, density, stoichiometry) relevant for the ESNII prototypes.

II – EUROPEAN CATALOG ON $(U,Pu)O_2$ PROPERTIES

In the ESNII+ project (WP 7, *safety fuel*), the fuel properties required for all European FR fuel performance codes were listed and the range of interest for each input parameter of these properties was defined (density, temperature, O/M, Burn-Up, Pu content, microstructure).

A state of the art report was then produced and the conclusions were used to define the experimental program. The European catalog issued in October 2017 collects by property: a bibliographic study, the properties measured in the ESNII + project and recommendations on the laws to be used. Table 1 summarizes the contents of this new catalog which follows the one issued in 1991.

		State of the art	Recommandation	New measurements
2	Lattice parameter	X	X	
3	Thermal conductivity	X		X
4	Melting point	X	X	X
5	Specific heat	X	X	X
6	Enthalpy of fusion	X	X	
7	Emissivity	X	X	
8	Theoretical density	X	X	
9	Thermal expansion	X	X	
10	Elastic constants	X	X	X
11	Brittle-to-ductile transition temperature	X	X	
12	Yield stress	X	X	
13	Ultimate stress	X	X	
14	Thermal creep	X		
15	Diffusion/migration of pores and fission gas bubbles	X		
16	Diffusion/migration of fission gas	X		
17	Diffusion/migration of U and Pu	X	X	
18	Diffusion/migration of oxygen	X		
19	Oxygen potential	X	X	
20	Grain growth in MOX	X	X	

Table 1: Content of the european catalog on MOX properties – ESNII+ project - 2017.

III – MATERIALS SELECTION FOR PROPERTIES MEASUREMENTS

Within the experimental program, the selection of available fuel was the starting point. The table below gathers main characteristics of fresh and irradiated fuels for both projects ESNII+ and ESFR-SMART.

FRESH FUEL	Pu content		24.5	28.4	32.7	40	45
			Phenix-internal core	CAMP99 Phenix external core	CAPRA4	TRABANT2	TRABANT2
IRRADIATED FUEL	Pu content	19.8	23.3	28.4			40
		NESTOR Phénix	PAVIX-155 Phénix	MYOSOTIS-12 Phénix			TRABANT 2 HFR
	Burn Up	11 at%	13 at%	16,34 at%			6 at%

ESNII+ (2013-2017)	ESFR-SMART (2017-2021)

Table 2: Characteristics of fresh and irradiated fuels $(U,Pu)O_x$ for properties measurements in ESNII+ & ESFR-SMART projects.

Fresh and irradiated FBR MOX fuels have been characterised and their properties measured. This work was already completed for the ESNII+ program and is on-going for ESFR-SMART.

The fresh fuel with 24.5 % Pu content was a standard Phenix fuel and characterisations have shown a microstructure which can be said to be homogeneous at micro-scale from the point of view of plutonium dispersion.

The irradiated fuel was issued from the NESTOR 3 irradiation experiment performed in the Phénix reactor in the 1980s. The post-irradiation examinations reveal the presence of columnar grains and of a central hole, formed with the mechanism of evaporation & condensation taking place already at the very start of the irradiation. Further analyses have shown the radial redistribution of Pu due to the same mechanism, with higher contents around the central hole. The radial profile of Am, Nd and Ce are similar to that of Pu. A grains subdivision, similar to the formation of the HBS in LWR fuels, was observed at the pellet periphery with a thickness of about 100 µm at the maximum flux plane (MFP).

More details are provided in Tables 3 and 4 for the fuels which properties measurements are presented in this paper.

Project	Composition	Synthesis	Pu (mol%)	O/M	Density %TD
Phenix internal core	$U_{0.765}Pu_{0.235}O_{1.978}$	MM	23.5%	1.978	94.6
Phenix internal core	$U_{0.765}Pu_{0.235}O_{2.00}$	MM	23.5%	2.00	94.6
Trabant 2/2 14KB0037	$(U_{0.6}Pu_{0.4})O_{1.995}$	MM	39.71%	1.995	94.1
Trabant 2/1 14KB0038	$(U_{0.6}Pu_{0.4})O_{1.96}$	MM	39.71%	1.960	94.77
Trabant 2/3 14KB0039	$(U_{0.55}Pu_{0.45})O_{1.99}$	SG	45.11%	1.990	93.00
Trabant 2/3 14KB0040	$(U_{0.55}Pu_{0.45})O_{2.00}$	SG	45.11%	2.000	92.89

Table 3: Characteristics of fresh $(U,Pu)O_x$, synthesis by mechanical milling (MM) or sol-gel (SG)

Axial position	MAXIMUM FLUX PLANE	TOP FISSILE COLUMN
Burn-up (at%)	13	10
Lineic Power (W/cm)	377	287
Irradiation temperature max at beginning of life (K)	2550	2290
Irradiation temperature min (K)	2090	1730
Density, %TD	97.09	96.6

Table 4: Irradiation conditions and characteristics of irradiated fuels – NESTOR 3 experiment.

IV – PROPERTIES MEASUREMENTS

Samples were prepared from fresh fuel pellets and from irradiated fuels segments, and characterized for their density, O/M, microstructure and composition. Then properties were measured for the ESNII+ fuels and the results are presented in this paper.

For this paper, we have chosen to detail the data instead of any experimental device used for the measure.

Melting temperature

The results of the fresh fuels melting temperatures determinations are summarized in Table 5. The average value determined for the stoichiometric fuel (3040± 30K) is in excellent agreement with the value determined by Böhler [1] for MOX with 25 wt.% Pu: 3045± 30 K. Literature data for hypostoichiometric MOX is not available.

Fuel: Phenix internal core	First Determination (K)	Second Determination (K)	Third Determination (K)	Average (K)
$U_{0.765}Pu_{0.235}O_{2.00}$	3053 ± 30	3035± 30	3036± 30	3040 ± 30
$U_{0.765}Pu_{0.235}O_{1.978}$	2965± 30	2992± 30	2995± 30	2984 ± 30

Table 5: Melting temperatures (solidus)

As shown in Figure 1, the CALPHAD evaluation under estimates solidus [2]. The existing law for melting temperature should be revised following all these and other recent results [1]. Updated calculations will be launched and a new law provided as soon as possible.

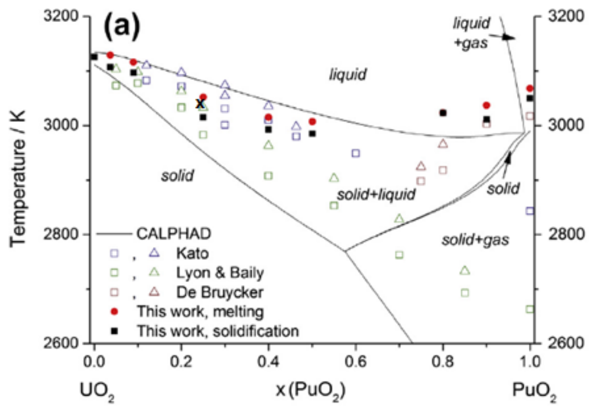

Figure 1: Melting temperature of $(U,Pu)O_2$ according to [1]. The measurement result obtained for the Phenix fuel is shown with the symbol "X"

Thermal expansion

Figure 2 shows a comparison between the recommended values from Martin [3] and our experimental data for unirradiated stoichiometric fuel.

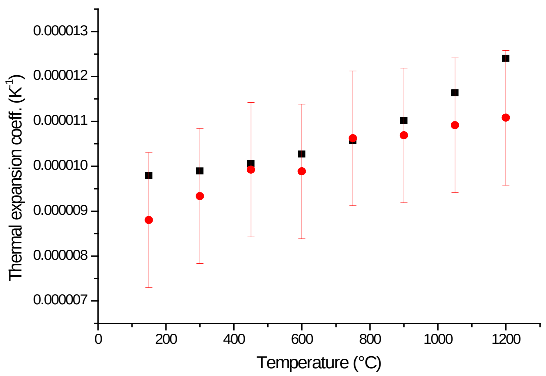

Figure 2: Comparison of the thermal expansion coefficients from Martin's recommendation (squares) with our experimental data (dots).

Previous studies on the thermal expansion of hypostoichiometric $(U,Pu)O_{2-x}$ material with plutonium content in the range 19.1-25% have been compiled and analysed by Martin and a relationship between the thermal expansion and the O/M ratio: $\alpha=10.38(1+3.98\,x)$, where α is the average constant in units of 10^{-6} K^{-1} and x the deviation from stoichiometry.

However Martin's law is based on the assumption that the thermal expansion of MOX is identical to that of UO_2 with correction of stoichiometry. Therefore the Martin law does not take into account the effect of the Pu content and is applicable for an O/M between 1.94 and 1.995 and a temperature lower than 1800K.

The most recent law of Kato [4] was established on the MOX taking into account the Pu content and the O/M until 1923K.

It will be important to continue measurements at higher temperatures and on a wider range in Pu content. Concerning the diphasic system, it is worth mentioning that the system U-Pu-O for high content of plutonium appears more complex than initially reported. Indeed the ternary phase diagram U-Pu-O has recently been revisited [5, 6] and it has been shown that for high concentrations of plutonium 0.20 < Pu< 0.62, there is a gap of miscibility. A fuel entering this composition decomposes into two fluorite-type phases, one stoichiometric and a second one hypostoichiometric. This recent work might explain the behavior of the two compounds at high temperature.

Heat capacity

Fresh fuel :

The specific heat of unirradiated fuels obtained during the ESNII+ Project and a comparison to the recommendation of Duriez [7] is shown in Figure 3.

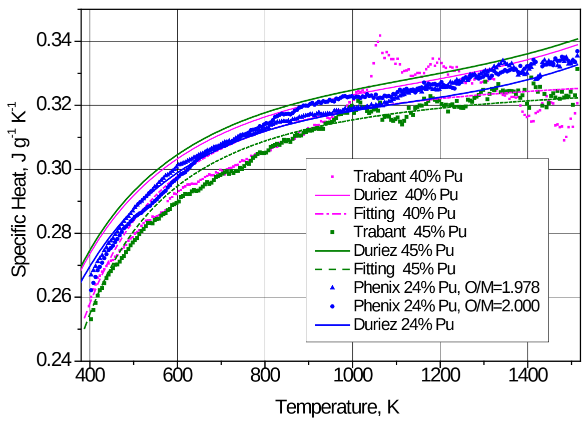

Figure 3 : Specific heat of unirradiated fuels obtained during the ESNII+ Project and comparison to the recommendation

Taking into account the experimental uncertainties (relative uncertainty of 7 %), the new specific heat values can be considered as consistent with the litterature data.

However it must mentioned that the effect of Pu content is expected at high temperature as heat capacity of PuO_2 is increasing above 1800K. Indeed additional measurements above 2000K will be helpful for a validation of the Cp law.

Irradiated fuel :

The specific heat of the NESTOR 3 samples with 10 and 13 at.% burn-up as a function of temperature are shown in Figure 4 and is compared to the fresh fuel value calculated following the recommendation of Duriez et al. [7].

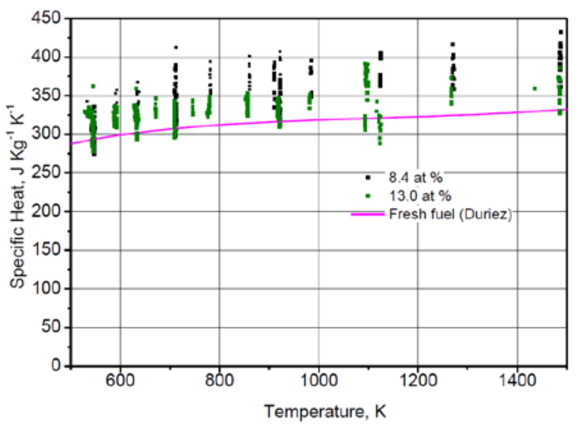

Figure 4: Specific heat of the irradiated NESTOR 3 fuel and comparison to the recommendation of Duriez [7].

The irradiated fuel specific heats follows the fresh fuel trend, but the value is in average about 14 % higher at 10 at.% burn-up and about 7 % higher at 13 at.% burn-up. The difference between fresh and irradiated fuel is of the order of magnitude of the experimental uncertainty. Once again, measurements at higher temperature are required.

Thermal diffusivity and thermal conductivity

The thermal conductivity of the fresh and irradiated fuels was deduced from the measured thermal diffusivity, the density predicted with the fresh fuel characteristics and the specific heat of the fresh fuel.

Fresh fuel :

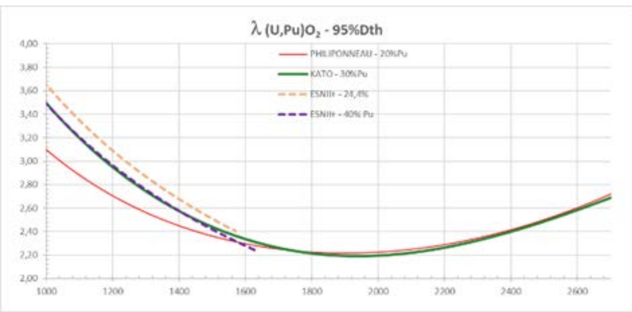

Figure 5: Thermal conductivity of unirradiated fuels obtained during the ESNII+ Project and comparison to the recommendation of Philipponeau and Kato.

The thermal conductivity of the Phenix sample (24.4%Pu, 95 % TD) is compared in Figure 5 to the recommendation on MOX of Philipponeau with 20 % Pu [8] and Morimoto for with 30 % Pu [9]. The thermal conductivity of the Phenix sample is higher than the recommendations from Philipponeau especially at low temperature.

Trabant stoichiometric fuels obtained by mechanical milling with 40% Pu and Trabant stoichiometric fuels obtained by sol-gel with 45% Pu were also measured in the framework of the ESNII+ Project. The thermal conductivities for the Pu contents of 40 and 45% are very close and 6% lower than the conductivity of the Phenix fuel with 24% Pu, but remain higher than the recommendation of Philipponeau. An effect of the Pu content on the thermal conductivity, as suggested by the measurements of Sengupta [10], Vasudeva Rao [11] and Kato [12] is therefore observed, specially for hypostoechiometric fuels.

All these results need to be completed for higher temperatures (1600K up to the melting point).

Irradiated fuel :

The thermal diffusivity was measured in 3 radial positions:

- “cladding”, position 0.6 mm from cladding, with estimated irradiation temperature of about 1510K

- “middle” position 1 mm from cladding, with estimated irradiation temperature of about 1750K

- “center” position 1.4 mm from cladding, with estimated irradiation temperature of about 1900K

The results obtained for the fuel with 13 at. % burn-up are shown in Figure 6. No large difference is observed between the three investigated radial positions, a slight decrease of thermal conductivity at the same temperature is observed from the centre of the pellet to the periphery which is associated with an increase of burn-up and an increase of plutonium content (21.3%Pu near central hole, 16.5%Pu at 0.6R, 20%Pu at R).

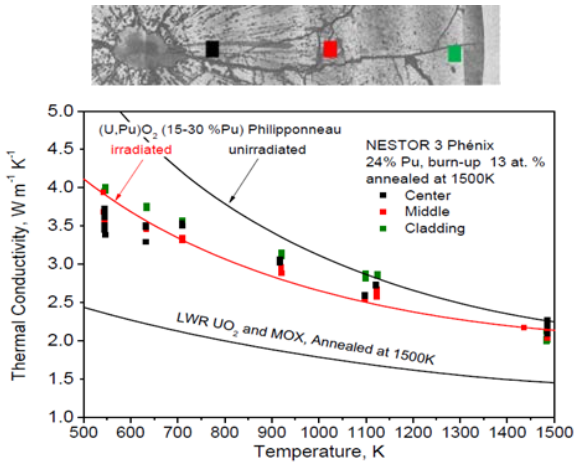

Figure 6: Thermal conductivity of the irradiated fuel (NESTOR 3 in Phenix reactor) obtained during the ESNII+ Project and comparison to the recommendation of Philipponeau.

The knowledge on the thermal conductivity of irradiated FBR MOX is currently very limited. Only one publication is available [13] providing an experimental result which is surprising: no degradation of thermal conductivity with burn-up was observed, within the relative experimental uncertainties which were estimated to be up to 20 %. Philipponeau published a recommendation based on a review of fresh fuel results where the effect of burn-up was quantified by doping with simulated fission products. The formula of Philipponneau includes the effect of solid fission products but no effect of irradiation damage.

At the burn-up of 13 at. %, the thermal conductivity of the irradiated NESTOR 3 fuel was found to be significantly higher than for LWR UO_2 or MOX fuels with similar burn-up. The impact of the irradiation temperature, radiation damage concentration, plutonium content, fission gas atoms and fission products was considered by comparison with the predictions of correlations available for irradiated LWR fuel. It was shown that the correlations for LWR fuels can not be adapted to FBR fuel even by adjusting the irradiation temperatures to levels allowing for a complete recovery of radiation damage and release of the fission gas atoms from the fuel matrix.

Measurements in a higher temperature range would be important for FBR fuel (up to 2700K) but the current set-up available for irradiated fuels is limited to a maximum temperature of 1600K. This maximum temperature was however not the limiting factor for the current measurements, because the samples started to fragment slightly above 1500 K.

Young Modulus

Fresh fuel :

The Young's modulus was measured for the un-irradiated stoichiometric Phenix and Trabant MOX fuels. No porosity correction was applied, as the density of the sample is very close to 95 % TD. The results are given in Table 6. The Young's modulus for the sample damaged by auto-irradiation (not annealed after storage) is about 5 % lower than for the annealed sample.

Sample Description	Pu content (Pu/(U+Pu) %)	O/M	Young´s modulus (GPa)	uncertainty non-annealed (GPa)
Non-annealed Phenix Fuel	23.5	1.978 [Sta17a]	195.2	1.5
Annealed Phenix Fuel	23.5	2.00 [Sta17a]	204.6	1.9
Non-Annealed TRABANT Fuel	45.0	1.99 [Sta17b]	190.0	8

Table 6: Young’s modulus values measured in the framewok of ESNII+ project on Phenix (23.5%Pu) and TRABANT (45%Pu).

A literature review has shown that the addition of PuO_2 to UO_2 causes a moderate [14] or even negligible [15] increase in Young’s modulus. Applying the recommendation of Gatt [16] for UO_2 with 5% porosity, we obtain a young's modulus of 193 GPa. In MATPRO [17], a 3% increase in Young’s modulus due to an addition of 20% PuO_2 to UO_2 was recommended, which leads to a value of 200 GPa for our Phenix fuel. The result obtained for the Phenix fuel is therefore consistent with this literature review.

V –CONCLUSION AND PERSPECTIVES

The ESNII + project and then the ESFR-SMART project make it possible to acquire property measurements on MOX fuels for fast neutron reactors. A wide variety of materials has been taken into account with Pu content of 20 to 45%, stoichiometries and varying densities.

The accuracy of the measurements obtained during the ESNII+ and ESFR-SMART projects, associated with a precise characterization of the fuels, now makes it possible to review the properties used as input for the fuel performance evaluations.

A new FBR MOX properties catalogue was issued in 2017 and will be updated in 2021 as a result of measurements that will be made especially at temperatures above 1600K.

The ultimate goal remains to produce a recommendation for each property that takes into account all the characteristics of the material, based on a critical review of the available data completed with new experiments focused on the properties requiring improvements.

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REFERENCES

1. R. BÖHLER, M.J. WELLAND, D. PRIEUR, P. CAKIR, T. VITOVA, et al., J. Nucl. Mater. 448(1-3) (2014) p. 330–339.
2. C. GUENEAU, “Challenges in predicting irradiated nuclear fuel thermodynamics”, NUMAT 2018, Seattle.
3. D.G. MARTIN, J. Nuc. Mater. 152 (1988) p. 94.
4. Journal of Nuclear Materials 469 (2016) 223-227
5. R.C. BELIN, M. STRACH, T. TRUPHÉMUS, C. GUÉNEAU, J.-C. RICHAUD, et al., J. Nucl. Mater. 465 (2015) p. 407-417.
6. R. VAUCHY, R.C. BELIN, A.-C. ROBISSON, and F. HODAJ, J. Nucl. Mater. 469 (2016) p. 125-132.
7. C. DURIEZ, J.P. ALESSANDRI, T. GERVAIS, and Y. PHILIPPONNEAU, J. Nucl. Mater. 277 (2000) p. 143-158.
8. Y. PHILIPPONNEAU, J. Nucl. Mater. 188 (1992) p. 194-197.
9. K.Morimoto J.Nucl.Mater. 443 (2013)286–290
10. P.R. VASUDEVA RAO, JNM 348 (2006) 329–334
11. A.K. SENGUPTA JNM 385 (2009) 173–177
12. K. MORIMOTO, M. KAto, FR09, Kyoto, 07-11 December 2009 IAEA-CN-176/07-20P The influence of Pu-content on thermal conductivities of (U, Pu)O2 solid solution
13. K. YAMAMOTO, T. HIROSAWA, K. YOSHIKAWA, K. MOROZUMI, and S. NOMURA, J. Nucl. Mater. 204 (1993) p. 85-92.
14. C.H. NOVION, B. AMICE, A. GROFF, Y. GUERIN, and A. PADEL, Nucl. Metall. 17 (1970) p. 509.
15. D.G. MARTIN, High Temp.-High Press. 21 (1989) p. 13.
16. J.-M. GATT, Y. MONERIE, D. LAUX, and D. BARON, J. Nucl. Mater. 336 (2005) p. 145.
17. L.J. SIEFKEN, E.W. CORYELL, E.A. HARVEGO, and J.K. HOHORST, *SCDAP/RELAP5/MOD 3.3 Code Manual, MATPRO - A Library of Materials Properties for Light-Water-Reactor Accident Analysis, U.S. Nuclear Regulatory Commission Report NUREG/CR-6150 Vol. 4 (INEL-96/0422), Rev. 2, January 2001.*