A STUDY OF THE UO_2/Gd_2O_3 COMPOSITE FUEL

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Abstract

Composite fuels or targets are considered as possible candidates for use in various applications (advanced fuels, burnable poisons, minor actinide incineration, increased plutonium consumption...). This paper summarizes the results of studies performed on UO_2/Gd_2O_3 composite fuels.

The use of a burnable poison present within the fuel is being considered in order to increase the length of irradiation cycles beyond 12 months in French PWRs without increasing the concentration of soluble boron in the coolant. Furthermore, to extend the efficiency of the poison by slowing its gadolinium consumption down, a study was led using gadolinia in the shape of 300 μm diameter macrospheres, dispersed within the UO_2 fuel.

The first stage of the studies involved manufacturing and characterizing the microstructure and sinterability of a UO_2 matrix 12 wt% gadolinia composite, with Gd_2O_3 macrospheres 300 μm in diameter. The second stage consisted in comparing the conductivity of the composite to that of stoichiometric UO_2 and a gadolinia-doped UO_2 containing the same proportion of gadolinium. Furthermore, composite reaction with water under PWR conditions has been studied.

1. INTRODUCTION

In order to achieve irradiation cycles exceeding 12 months in French PWRs, it is planned to use burnable poisons within the fuel, such as for example gadolinium oxide. Moreover, in order to prolong the efficiency of the poison, a study was conducted using gadolinia in the shape of 300 μm diameter macrospheres, homogeneously dispersed within the urania matrix.

This paper presents the work carried out on a composite fuel containing 12 wt% of gadolinia macrospheres, the objective being to study the properties such as its sinterability, its thermal conductivity and its reaction with water under PWR conditions, compared both to pure UO_2 and gadolinia-doped UO_2 containing the same proportion of gadolinium .

2. DESCRIPTION OF THE BATCHES STUDIED

The gadolinia macrospheres were manufactured by a granulation process [1]. All the composite batches were elaborated using the same UO_2 powder which constitutes the matrix, and using similar forming and sintering conditions (uniaxial pressing at 350 MPa-1700°C for 2 hours in H_2 + 2 vol. %H_2O).

The manufacturing objectives consisted on the one hand in obtaining a high density material free of any cracks likely to affect its intrinsic properties, and on the other hand, to preserve the initial quasi-spherical shape of the inclusions after pressing.

In order to avoid distorting the shape of the Gd_2O_3 macrospheres during pressing, it was found useful to consolidate them by a preliminary heat treatment before mixing them with the UO_2 powder. Three different batches were characterized in order to study the effects of the preliminary consolidation of the macrospheres on the final microstructure, the sinterability and the thermal conductivity of the composite structure.

The various batches studied are described in Table 1.

3. CHARACTERIZATION OF THE BATCHES

3. 1. Density

The relative densities (d/d_{th}) are shown in Table 2. The density of the composite pellets decreases as the preliminary consolidation temperature of the Gd_2O_3 macrospheres increases.

3. 2. Porosity

The main results are shown in Table 2. The open porosity increases significantly with the consolidation temperature of the macrospheres. As stated in the literature [2-9], batch C, initially containing dense macrospheres, appears to be the worst from the point of view of density as well as open porosity.

TABLE 1

Batch	Conditions of the preliminary heat treatment of macrospheres	Diameter of macrospheres before pressing (μm)
A	none	360
B	1200°C-1 hour in air atmosphere	360
C	1700°C-2 hours in (H_2+2vol% H2O) atmosphere	300

TABLE 2

Batch	Sintering Temperature (°C)	Gd_2O_3 content (%)	Density		Porosity	
			d/d_{th} (%) before sintering	d/d_{th} (%) after sintering	Open P_o(%)	Total P(%)
A	1700	12	53,75	94,2 ± 0,3	0,41 ± 0,10	5,81 ± 0,27
B	1700	12	54,19	94,0 ± 0,2	0,63 ± 0,13	5,95 ± 0,17
C	1700	12	56,38	93,6 ± 0,4	2,48 ± 0,21	6,39 ± 0,45
pure UO_2	1700	-	51,9	95,7 ± 0,2	0,10 ± 0,05	4,30 ± 0,13

3. 3. Dilatometric analyses

In order to compare the densification kinetics for pure UO_2 and the UO_2 matrix of batches A and C, the density of the matrix was calculated in the $800°C$-$1600°C$ temperature range using the following equation :

$$\frac{1}{d_{m/c}} = \frac{1}{d_c(1-\eta)} - \frac{\eta}{d_{Gd_2O_3}(1-\eta)}$$

where η is the weight fraction of Gd_2O_3 (= 12 wt%),

$d_{m/c}$ is the density of the UO_2 matrix within the composite,

d_c is the density of the composite (measured),

$d_{Gd_2O_3}$ is the density of Gd_2O_3 (measured).

The densification kinetics for pure UO_2 and UO_2 matrix of batches A and C are compared in Fig. 1. The results show that the Gd_2O_3 macrospheres significantly hinder the densification of the matrix.
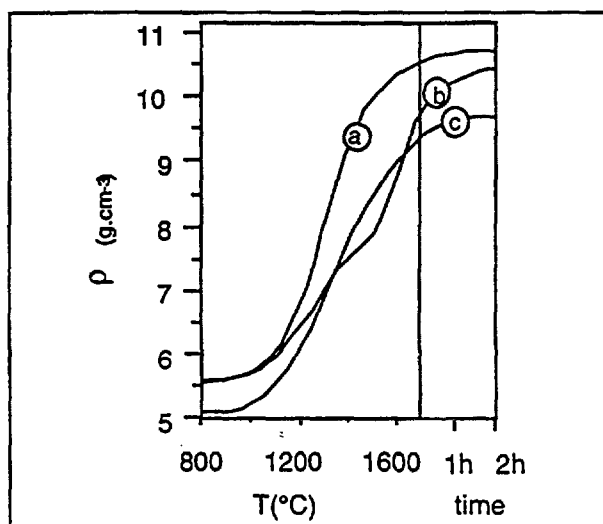

FIG. 1.   *Density as a function of temperature and time*

3. 4. Microstructural Observations

The observations performed using optical and scanning electron microscopes reveal how the macrospheres are distorted during the pressing stage, the appearance of microcracks and heterogenous density zones within the matrix, as well as the interconnected porous zones around the macrospheres.

- *Shape of macrospheres*

Batch A contained Gd_2O_3 macrospheres which showed extensive flattening in a direction perpendicular to the pressing axis (Fig. 2a). This clearly indicates that the cohesion is inadequate. In batches B and C, the shape of the macrospheres is improved due to the preliminary consolidation by heat treatment of the Gd_2O_3 macrospheres at 1200°C and 1700°C respectively for batches B and C (Fig. 2b).

- *Cracking of the UO_2 matrix*

- Contrary to batches B and C, microcracks were observed in the matrix of batch A (Figs. 2a, 3a, 3b).

- *Macrosphere-matrix interface*

Although absent from batch A, an interconnected porous zone was observed around the macrospheres in the batches B and C. This zone was larger for batch C than for batch B (Figs 3c and 3d). Examination of polished samples indicated a diffusion zone at the macrosphere-matrix interface (Fig. 3a). The thickness of the diffusion zone was evaluated at approximately 20 μm using a electron probe microanalyser.

Figure 4 represents the macrosphere-matrix interface structure. Two different phases have been identified using a electron probe microanalyser at the macrosphere-matrix interface. The first phase, adjacent to the macrosphere exhibits a 4 μm grain size. According to the phase diagram established by Beals [10] (Figure 5), it appears very probable that this phase is UGd_6O_{11}. The second phase, consisting mainly of submicronic grains, corresponds to the $(U_{1-x}, Gd_x)O_{2-y}$ solid solution, the concentration of gadolinium decreasing steadily down to 0% (UO_2 matrix).

- *Heterogenous density in the matrix*

The density of the matrix is not homogeneous. As stated in the literature, certain very dense zones were observed in the matrix particularly between the closely spaced macrospheres, especially for batch C, and often adjacent to porous zones [11, 12]. Additionally, dense regions of the matrix often presented a large grain microstructure (Fig. 3e) [11, 13-15].

3. 5. Discussion

The dilatometric analyses show in all cases that the presence of macrospheres hinders the densification of the matrix. This hindrance is frequently attributed to the density variations noted in the matrix. Moreover, the differential thermal expansions between the two constituents during cooling can generate thermal stresses which are the cause of the microcracks in the matrix. The specimens including non consolidated macrospheres (batch A) exhibit a microcracked UO_2 matrix due to the difference between the thermal expansion coefficients of the two phases below 600°C. On the other hand, in the specimens including Gd_2O_3 macrospheres previously consolidated or even densified, a porous zone was observed around the macrospheres.
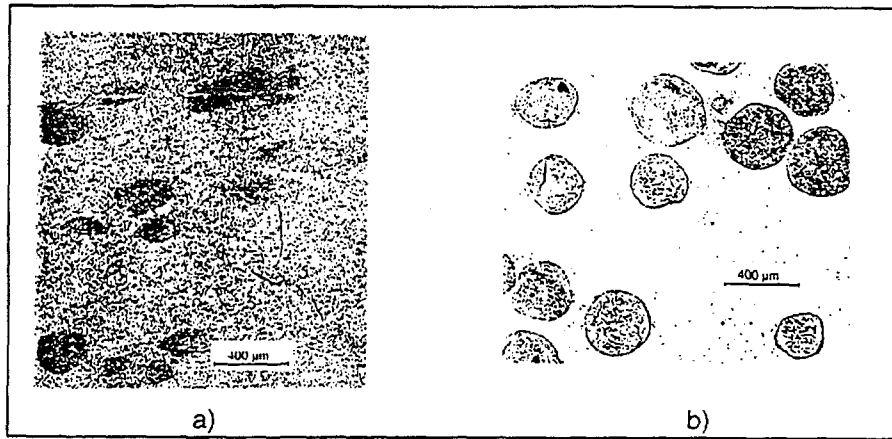
FIG. 2.   Shape of macrospheres in the sintered pellets: a) batch A, b) batch B
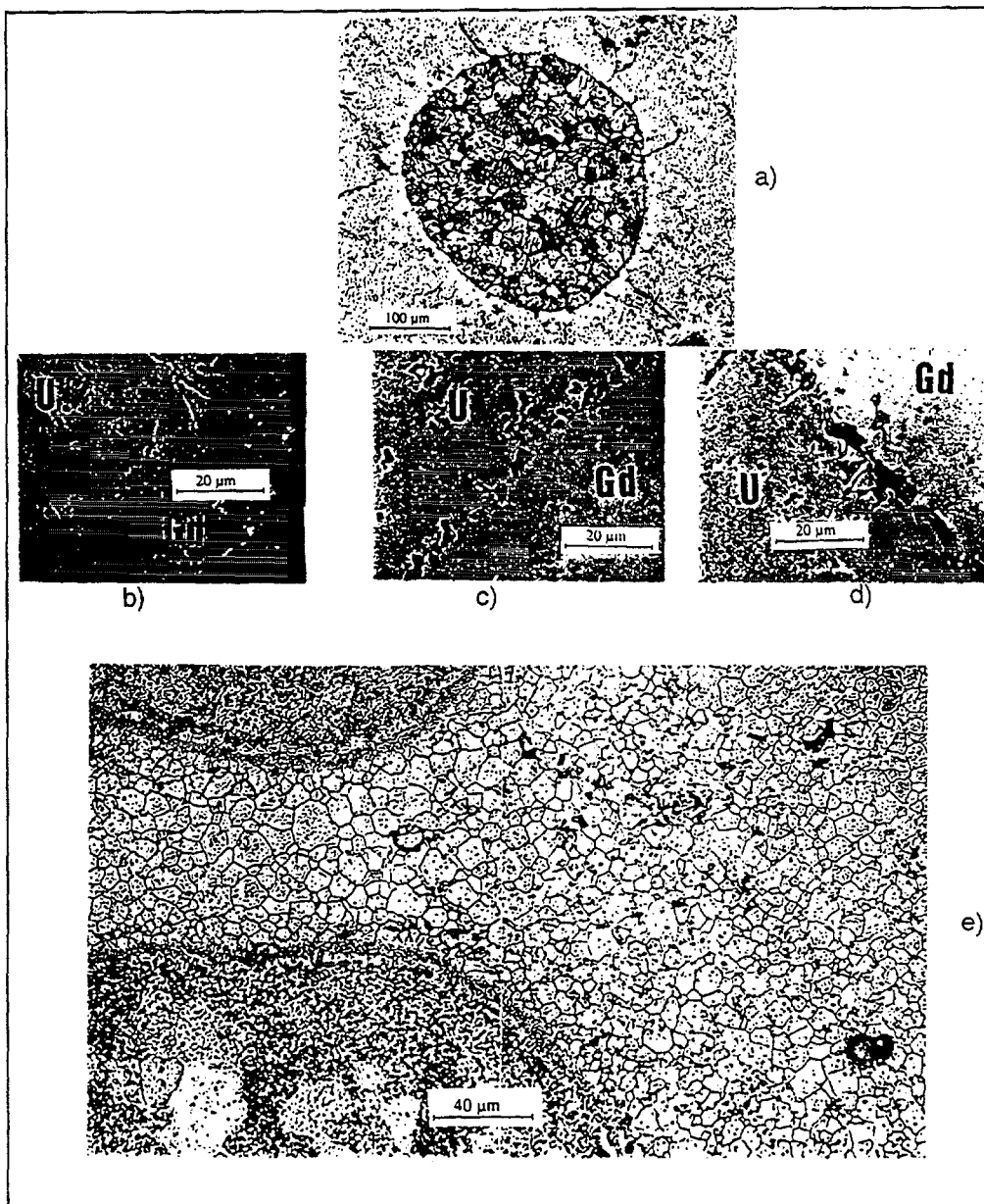

FIG. 3.   a) Cracking of the matrix (batch A); b), c), d) macrospheres - matrix interface for batches A, B, C; e) microstructure of UO₂ matrix.
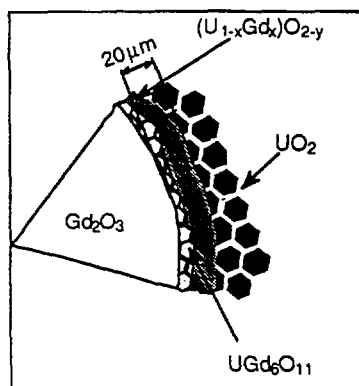
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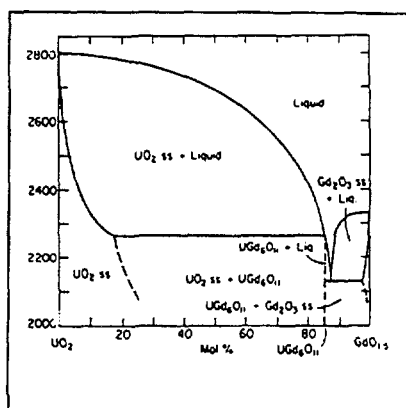FIG. 4.   Schematic representation of macrosphere - matrix interface.

FIG. 5. UO_2-Gd_2O_3 phase diagram [15].

The effect of inclusions and heterogeneities on the sintering process has been the subject of many theoretical and experimental studies [2-9]. It has been widely observed that the sinterability of a polycristalline ceramic powder used as the matrix can be reduced significantly by the presence of a rigid inclusion phase. In fact, during the uniaxial pressing stage, heterogeneities are produced in the matrix, particularly between the closely spaced macrospheres. During the sintering process, these prematurely dense regions form, with the near-touching macrospheres, a rigid, continuous network which can substantially reduce the overall densification of the composite matrix, this hindrance is all the more marked if the macrospheres are unable to densify (batch C).

4.   THERMAL CONDUCTIVITY

The thermal properties of stoichiometric UO_2 and gadolinia-doped UO_2 are relatively well known [16-19]. The same cannot be said for the UO_2/Gd_2O_3 composite fuel. The objective is therefore to calculate the thermal conductivities of the composite batches A and B, in order to be able to compare them with the gadolinia-doped UO_2 including 12 wt % of Gd_2O_3.

The thermal conductivity (λ) is obtained from the product of the thermal diffusivity (a), the density (ρ) and the specific heat (Cp).

It is known that the addition of gadolinia to UO_2 has a negative effect on the thermal conductivity. Figure 6 shows that the thermal conductivity of the gadolinia-doped UO_2 is in fact lower than that of pure UO_2.
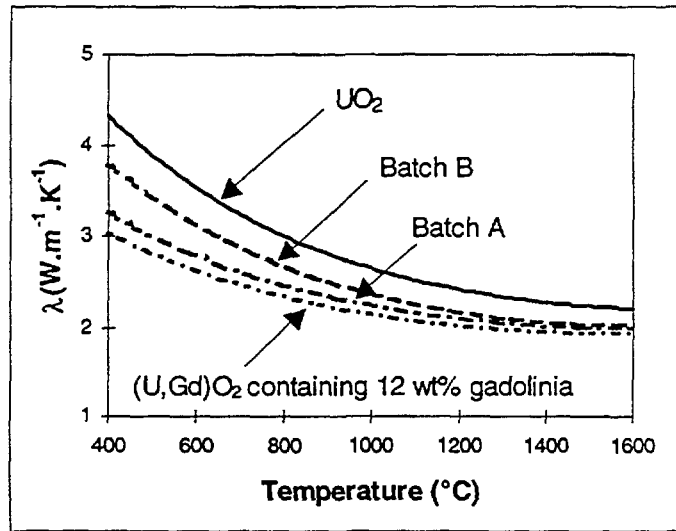

FIG. 6.   Comparison of the thermal conductivities.

The measurements taken using UO_2/Gd_2O_3 are similar.   The addition of Gd_2O_3 macrospheres, with a lower thermal conductivity than UO_2, within the 400°C-1600°C temperature range, reduces the overall conductivity of the fuel. To illustrate this, it can be seen that the conductivities of composite batches A and B are respectively 10% and 14% lower than for stoichiometric UO_2 with the same density at 1000°C.

Within the temperature range investigated (400°C-1600°C) and for the same proportion of gadolinium, our measurements show on the one hand that in all cases, for the same gadolinium content, the thermal conductivity of the UO_2/Gd_2O_3 composite is better than that of a stoichiometric gadolinia-doped UO_2 (i.e. 10% increase at 1000°C), and on the other hand that the thermal conductivity of batch A is lower than that of batch B. This result therefore shows the high sensitivity of thermal conductivity to the presence of microcracks in the matrix, compared with porosity located around the macrospheres.

5.   REACTION WITH WATER

Preliminary tests show that gadolinia reacts with water under PWR conditions (i.e. 350°C and 155 bar) to produce a gadolinium hydroxide $Gd(OH)_3$ which results in a considerable swelling of the material [1]. The same can be said for the UO_2/Gd_2O_3 composite fuel. Tests performed on the composite show a strong affinity to water which leads to a destruction of the pellets. This incompatibility with water under PWR conditions for the composite pellets can be explained by the reaction of the peripheral gadolinia macrospheres with water to produce a hydroxide which in turn causes the macrospheres to swell and the matrix to crack (Fig. 7).
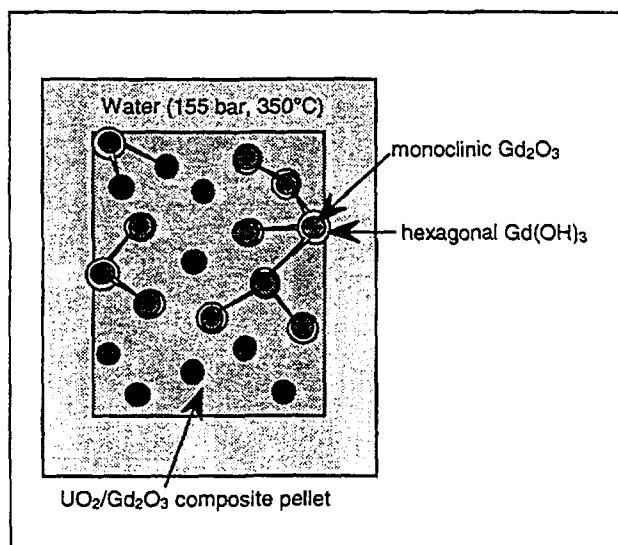
FIG. 7.   Schematic representation of the pellet destruction.

In order to suppress composite affinity to water whilst keeping gadolinium as the burnable poison in the form of macrospheres, it could be interesting   to find another gadolinium-based compound which can withstand aqueous corrosion.   Gadolinium orthoaluminate ($AlGdO_3$) would seem to be a likely candidate.

The Al_2O_3-Gd_2O_3 phase diagram in fact shows the existence of this orthorhombic structured compound (a = 525.0 pm, b = 530.2 pm, c = 744.7 pm) with a theoretical density of 7.44:

$$Al_2O_3 + Gd_2O_3 \quad 2\ AlGdO_3 \ .$$
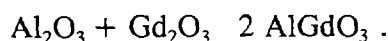
6.   CONCLUSIONS

The composite fuel consisting of 12 wt % gadolinia macrospheres (300 μm in diameter) homogeneously dispersed within urania matrix, certainly presents some advantage from a neutron point of view, but presents a certain number of problems in its elaboration. For example, it has been seen that the UO_2 matrix could crack under the effect of the differential thermal expansions between UO_2 and Gd_2O_3. But the essential problem is the distortion of the Gd_2O_3 macrospheres during the pressing process.   In order to avoid this problem, the macrospheres were subjected to a preliminary heat treatment in order to increase the cohesion before the pressing stage.

The results show the influence of the preliminary consolidation of the macrospheres by heat treatment. It was observed that:

- the density of the composite decreases slightly,
- the open porosity increases significantly,
- the size of the diffusion zone between the UO_2 and Gd_2O_3 remains constant and equal to 20 μm,

- the cracking of the matrix disappears,
- the thermal conductivity increases,
- an increasingly large interconnected porous zone appears around the macrospheres,
- more zones of varying density are observed ; a large grain microstructure is observed in the dense regions located between the closely spaced macrospheres.

The thermal conductivity measurements showed the improved thermal behaviour of the UO_2/Gd_2O_3 composite compared to the gadolinia-doped UO_2 containing the same gadolinium content. However, the strong affinity to water under PWR conditions revealed the limits of this fuel. An alternative solution, however, could consist in elaborating macrospheres of $AlGdO_3$, for example, as that compound does not react with water.

REFERENCES

[1]   BALESTRIERI, D., "Study and optimization of the composite nuclear fuel with burnable poison UO_2/Gd_2O_3,", Thesis : INSA, Lyon, No.95, ISAL 0061 (1995) 159 p.

[2]   SCHERER, G. W., "Sintering with Rigid Inclusions", *J. Amer. Ceram. Soc.*, Vol. 70, N° 10 (1987) 719-25.

[3]   EVANS, A. G., "Considerations of Inhomogeneity Effects in Sintering". *J. Amer. Ceram. Soc.*, Vol. 65, N° 10 (1982) 497-501.

[4]   HSUEH, C. H., "Sintering Behavior of Powder Compacts with Multiheterogeneities". *J. Mater. Sci.*, Vol. 21 (1986) 2067-72.

[5]   REEVE, K. D., "Non-Uniform Shrinkage in Sintering". *Am. Ceram. Soc. Bull.*, Vol. 42, N° 8 (1963) 452

[6]   LANGE, F. F., "Constrained Network Model for Predicting Densification Behavior of Composite Powders". *J. Mater. Res.*, , Vol. 2, N° 1 (1987) 59-65.

[7]   BORDIA, R. K.; Scherer, G. W., "Constrained Sintering: III. Rigid Inclusions". *Acta Metall.*, Vol. 36, N° 9 (1986) 2411-16.

[8]   WEISER, M. W.; De Jonghe, L. C. . "Inclusion Size and Sintering of Composites Powders"., *J. Amer. Ceram. Soc.*, , Vol. 71, N° 3 (1988) 125-127.

[9]   SUNDARESAN, S.; AKSAY, I. A., "Sintering with Rigid Inclusions : Pair Interactions". *J. Amer. Ceram. Soc.*, Vol. 73, N° 1 (1980) 54-60.

[10] BEALS, R. J.; HANDWERK, J. H. - WRONA, B. J., "Behaviour of Urania-Rare Earth Oxides at High Temperatures". *J. Amer.Ceram. Soc.*, , Vol. 52, N° 11 (1969) 578-81.

[11] SUDRE, O.; BAO, G.; FAN, B.; LANGE, F. F.; EVANS, A. G., "Effect of Inclusions on Densification: II, Numerical Model" *J. Amer. Ceram. Soc.*, Vol. 75, N° 3 (1992) 525-31.

[12] SUDRE, O.; LANGE, F. F., "The Effect of Inclusions on Densification: III, The Desintering Phenomenon".*J. Amer. Ceram. Soc.*, Vol. 75, N° 12 (1992) 3241-51.

[13] CAMERON, C. P.; RAJ, R., "Grain-Growth Transition During Sintering of Colloidally Prepared Alumina Powder Compacts". *J. Amer. Ceram. Soc.*, Vol. 71, N° 12 (1988) 1031-35.

[14] BROOK, R. J., "Pore-Grain Boundary Interactions and Grain Growth". *J. Amer. Ceram. Soc.*, Vol. 52, N° 1 (1969) 56-57.

[15] LAM, D. C.; LANGE , F. F., "Microstructural Observations on Constrained Densification of Alumina Powder Containing a Periodic Array of Sapphire Fibers". *J. Amer. Ceram. Soc.*, Vol. 77, N° 7 (1994) 1976-78.

[16]   HIRAI, M. "Thermal diffusivity of UO_2-Gd_2O_3 pellets" *J. Nucl. Mat.*, Vol. 173 (1990) 247-254.

[17]   FUKUSHIMA, S., "The Effect of Gadolinium content on the Thermal Conductivity of Near-stoichiometric $(U,Gd)O_2$ solid solutions". *J. Nucl. Mat.*, Vol. 105 (1982) 201-210.

[18]   HIRAI, M.; ISHIMOTO, S. "Thermal Diffusivity and Thermal Conductivities of UO_2-Gd_2O_3". *J. Nucl. Mat.*, Vol. 28, N° 11 (1991) 995-1000.

[19]   CHOTARD, A. ; MELIN, P. ; BRUET, B. ; FRANÇOIS, B., "Out of pile physical properties and in pile thermal conductivity of $(U,Gd)O_2$" IAEA - meeting Vienne 13-17/10/86.

DISCUSSION
(Questions are given in italics)

Comments:

Corrosion test perhaps too conservative because in the case of a failed fuel rod exposure to H_2O restricted by the cladding. Also the ex-reactor results that homogeneous $(U,Gd)O_2$ is resistant to corrosion does not apply to in-reactor, because of radiolytic oxidizing species. In the context of 12-18 month cycles, difference between composite and homogeneous corrosion may not be so great.

Besides the successful irradiation of this type of fuel more than 10 years ago in the BR3, was more recent irradiation performed?

Composite fuel has already been irradiated, but there is a very long time.