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Hafnium dioxide for porous and dense high-temperature refractories (2600 °C)

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Abstract

The VERDON project is devoted to the studies of fission products release in a hypothetical case of severe accident in a pressurized water reactor (PWR). The experiments will be performed on irradiated nuclear fuels: the fuel rod is heated with an induction furnace up to the melting point of the irradiated fuel (about 2600 °C). This furnace must be thermally isolated and some parts must resist to interaction with corium (magma of nuclear fuel and cladding) during a limited time. The refractory pieces needed to VERDON facility (dense and porous) are the subject of this work.

The dense pieces are made of hafnium dioxide doped with yttrium oxide in order to avoid cracking due to a phase transition which generates an important volumetric expansion. The ceramics obtained after sintering are dense (90%) and present mainly closed porosity. The porous pieces are prepared from a mixture of hafnium dioxide and a porous agent. After sintering, these pieces keep a satisfactory porosity (30–50 vol%) and do not crack during the phase transition.

Keywords: Refractory; Severe accident; Hafnium dioxide

1. Introduction

The VERDON facility is devoted to the study of irradiated fuel behavior in case of PWR severe accident for release and transport studies of fission products and actinides.

The VERDON project at CEA-Cadarache is devoted to the studies of fission products release and fuel degradation under severe accidents conditions. The tests will be performed on irradiated fuels up to the liquidus temperature of the irradiated fuels. The fuel sample will be heated in an inductive furnace under controlled atmosphere (steam, hydrogen, air, etc.) simulating the conditions of a hypothetical severe accident. The manufacturing of the refractory pieces (porous and dense) for this furnace is the subject of a Research Technological Thesis (DRT) in partnership with the French Atomic Energy Commission (CEA), the Center for Technology Transfer Ceramics (CTTC) and the National Industrial Ceramics School (ENSCI).

The refractory pieces can be separated into two families: the porous pieces allowing a thermal insulation and having a good dimensional stability at high temperature and the dense pieces, impermeable and resistant to hot creeping, and also having a good dimensional stability at high temperature.

In previous experiments on core fuel degradation, refractory materials were manufactured in thorium dioxide. This manufacturing process has been stopped and a palliative solution was to be found. A potential candidate is hafnium dioxide, which is one of the most refractory oxide materials ($T_{melting} = 2810$ °C), and well known to resist chemical interactions.

2. VERDON facility

The VERDON facility is devoted to the study of irradiated fuel behavior in case of PWR severe accident, and more particularly to the source term quantification (fission products (FP) and actinides release and transport).[1,2] This facility is the follow-up of the VERCORS facility which was operated at the CEA centre of Grenoble and whose experimental phase was stopped at the end of 2002. The new facility will be available mid-2008 at the CEA centre of Cadarache (building of two new hot cells).

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The specificities of the program which will be performed in the facility are the experimental representative conditions and the analytical approach: the tests will be performed with irradiated fuel samples coming from a nuclear power reactor operated by EDF (10–50 g of fuel depending on the tests), generally re-irradiated a few days at low power in an experimental reactor (MTR) in order to recreate the short half-life FP without inducing any in-pile release. The fuel sample will be heated in an inductive furnace under controlled atmosphere (steam, hydrogen, air, etc.) simulating the conditions of a hypothetical severe accident.

FP release kinetics will be measured on line by three complementary gamma spectrometers: one detector is focused on the fuel rod, another on the polar filter located just downstream the furnace, and the last one is devoted to the measurement of noble gases, typically the isotopes of xenon (^{133}Xe, ^{133}Xe, ^{135}Xe, created in the MTR reactor) and krypton (^{85}Kr created in nuclear power plant). Those detectors provide a very high sensitivity and excellent measurement dynamics.

Before and after each test, a gamma scanning equipment located in the cell beside the VERDON cell allows the FP balance on the fuel sample and on all the components of the loop after dismantling. At last, fission gases are collected in a storage tank located in a glove box, then measured by gamma spectrometry (^{133}Xe, ^{85}Kr) and by gas chromatography coupled with mass spectrometry (GC–MS) for the stable fission gases.

In this installation, refractory materials are needed to resist at very high temperature ($T = 2600\,^{\circ}C$) and to the interaction with "corium" during a limited time. New refractory materials are necessary to resist to these very aggressive conditions: high temperature, atmosphere, molten nuclear materials.

3. Experiment

3.1. Refractory materials and severe accidents test conditions

The refractory pieces of the VERDON furnace were manufactured in thorium dioxide for VERCORS experiments. This manufacturing process has been stopped and a palliative solution must be found.

These pieces must be made of ceramics oxides to resist to the different atmospheres of the experiments: oxidizing, steam, reducing. Only oxide materials can be used under oxidizing atmosphere or steam. Various oxides were studied and compared with the thorium dioxide. Table 1 presents and compares properties of well-known refractory oxides.

In VERDON facility, pieces can reach temperature until 2600 °C. So, an important characteristic for the refractory materials is the behavior at high temperature.

The melting point highlights that the best oxide, except for ThO_2 is HfO_2.

Hafnium dioxide and the zirconium dioxide both present the most important volumetric expansions at cooling but this is much less significant for hafnium dioxide.

Table 1
Thermo-physical properties of some refractory oxide materials.

Material	ThO_2	HfO_2	ZrO_2	Al_2O_3
Melting point (°C)	3370	2810	2710	2050
Volumetric expansion (%)	–	+3.4	+9	–
Young's modulus (room temperature) (GPa)	1.3	0.57	2	3.5
Thermal conductivity (beyond 1200 °C) ($W\,m^{-1}\,°C^{-1}$)	6	3	5	15

Young's modulus gives information on the mechanical properties at room temperature. Hafnium dioxide has a smaller value than thorium dioxide.

At least, hafnium dioxide presents the lowest thermal conductivity, which is a key point for the VERDON furnace application, especially for the pieces of the furnace which require a good thermal insulation. In addition this material is well known to resist chemical interactions with different other materials.[3] One important point concerns the possible interactions between the oxides and the susceptor in tungsten used for heating in VERDON facility.

These comparisons highlight that hafnium dioxide is the best candidate to replace thorium dioxide.

3.2. Dense pieces

Hafnium dioxide (HfO_2) presents three crystallographic forms each having their domain of stability according to temperature and pressure. These transformations take place at the atmospheric pressure[3–6] as follows:

$$\text{Monoclinic} \overset{1700^{\circ}C}{\leftrightarrow} \text{Quadratic} \overset{2600^{\circ}C}{\leftrightarrow} \text{Cubic} \overset{2800^{\circ}C}{\leftrightarrow} \text{Liquid}$$
$$\Delta V = +3.4\%$$

The monoclinic ↔ quadratic phase transition, observed during cooling or heating, is accompanied by a strong volumetric expansion (about 3.4%). This involves the cracking of the dense pieces. To avoid this cracking, the cubic phase of the hafnium dioxide can be stabilized by cations of valence lower than Hf^{4+}.

Different elements can play the role of stabilizing agent and allow stabilization of the cubic phase. The ceramic matrix undoubtedly does not need to be entirely stabilized in cubic form to resist to the volumetric expansion. Consequently a composite mixture of monoclinic and cubic phases should be enough to avoid cracking. In order to select the best stabilizing agent for hafnium dioxide ceramics for VERDON experiments, it has been necessary to study several phase diagrams (HfO_2–MgO, HfO_2–CaO, HfO_2–Y_2O_3), and especially to pay attention on liquidus and solidus temperatures.

The most promising system is HfO_2–Y_2O_3 system[7] (Fig. 1). Weak ratios of stabilizing agent allow realization of a mixture of a monoclinic and cubic phase. The yttrium oxide addition induces a weak decrease of the solidus temperature.

Table 2
Characteristics of HfO_2 and Y_2O_3 powders.

	Density	Specific surface ($m^2\ g^{-1}$)	Equivalent spherical diameter (nm)	Grain size (laser granulometer) (μm)
HfO_2	9.68	12.99	47.6	2
Y_2O_3	5.01	2.38	500	3

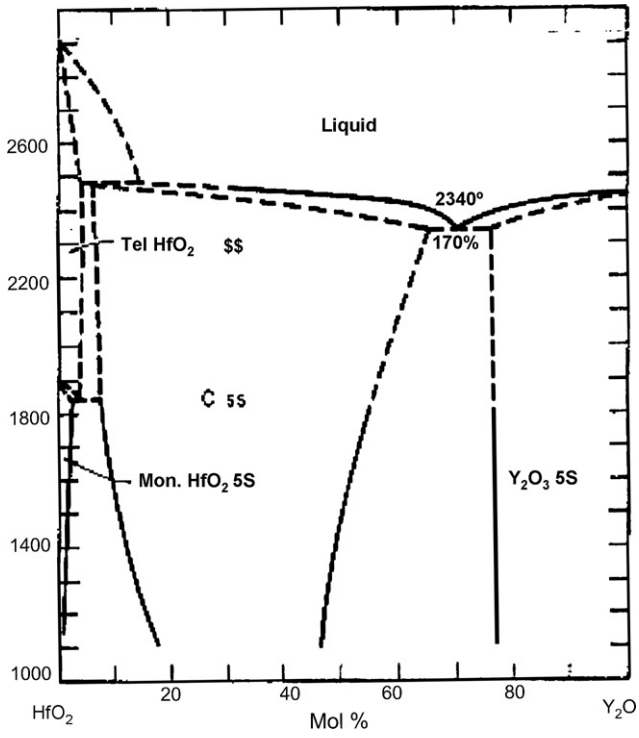

Fig. 1. HfO_2–Y_2O_3 phase diagram: solidus temperature.

Yttrium oxide is the best compromise between decrease of solidus temperature for severe accidents application and the practical set-up.

The main powder characteristics of hafnium dioxide (AREVA, CEZUS, France), and of yttrium oxide (PIDC, France) are shown in Table 2.

The hafnium dioxide powder is made of very small dense agglomerated particles. The sizes of yttrium oxide grains measured by BET method and laser granulometer are rather close. These characteristics of powders are in favour of a good ability to sintering.

From experimental point of view, various percentages of Y_2O_3 have been tested in order to find a compromise between high-temperature operation (up to 2600 °C) and cracking at intermediate temperature ($T = 1800$ °C). As said previously, the ceramic matrix does not need to be entirely stabilized in cubic form to resist the volumetric expansion. Three percentages of addition 3, 5 and 8 mol% yttrium oxide seems to be particularly interesting because they present the advantage of stabilizing the cubic phase in significant quantity.

Table 3
Porous agent properties.

Chemical nature	Size (μm)	T_g (°C)
Porous agent 1	85	15
Porous agent 2	25	108
Porous agent 3	10	Not given

3.3. Porous pieces

For porous pieces (porosity upper than 30% in volume), the ceramic material is expected to support the volumetric expansion caused by this phase transition without cracking. For this case the hafnium dioxide powder does not need any stabilizing agent.

The objective is to create porous pieces while adding to the ceramic matrix an element which is eliminated during thermal treatment and which generates large size and stable porosity. Three porous agents have been studied; the properties of these elements are presented in Table 3.

The VERDON porous pieces must play the role of thermal isolation and resist creep at high temperature. So the refractory materials must also both be very porous and preserve a good mechanical resistance at very high temperature (2600 °C). The porosity rate is then a compromise between the thermomechanical resistance of the pieces at high temperature and a good thermal insulation. Two porosity rates answer to these two conditions for VERDON facility: 30% and 50%.

3.4. Process

The dense and porous pieces are carried out by semi-isostatic pressing. Pressing requires a good flow of the powder and a homogeneous filling before pressing. Thus, it is necessary to granulate the powder to increase the flow rate. The operation of granulation consists in increasing the size of the particles to confer to them the desired properties of flow and filling of the mould. The granulation can be carried out in dry way by pelletization (formations of granules by pulverization of a solution) or in wet process by drying in a rotary evaporator or atomization. The best way to obtain dense pellets with HfO_2 powder is to granulate by pelletization.

Granules must be both resistant and ductile enough to be easily deformed during pressing and not to introduce a stable macroporosity during sintering. To obtain such a compromise, it is necessary to add to the powder some organic element, like binders and plasticizer.[8]

4. Results and discussion

4.1. Dense pieces

To evaluate the sinterability for HfO_2–Y_2O_3 ceramics, a dilatometric test was realized with 8 mol% of yttrium oxide.

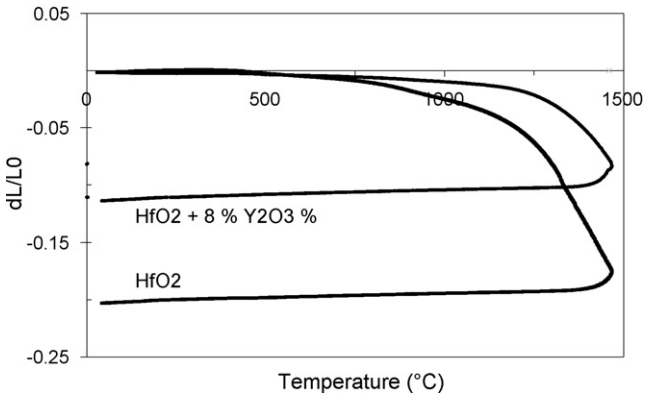

Fig. 2. Dilatometric curve for HfO_2 and HfO_2 + 8 mol% Y_2O_3.

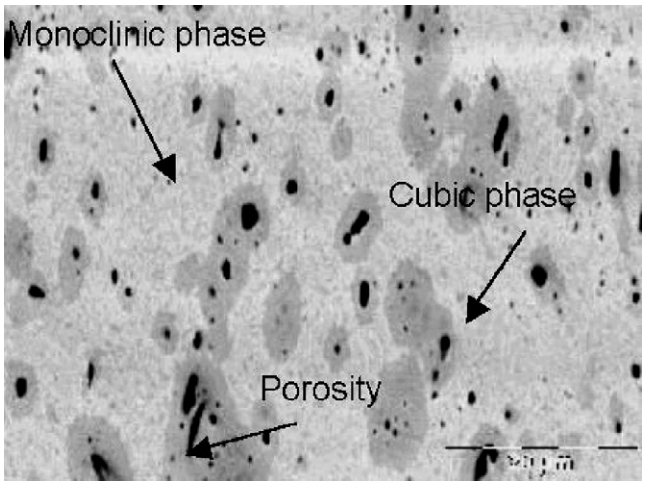

Fig. 3. Backscattered electron images of a HfO_2 and 5 mol% of Y_2O_3 sintered piece.

Results are compared with pure HfO_2 sample (see Fig. 2).

These curves highlight two points:

- If the rate of yttrium oxide is increasing, the shrinkage is decreasing,
- The addition of Y_2O_3 delays considerably the starting of sintering.

Various sintering cycles under air were tested with HfO_2 plus 3, 5 and 8 mol% of Y_2O_3 with the aim of evaluating the influence of temperature and time on compactness and open porosity.

The theoretical densities were estimated using the lattice parameters of the cubic phase and the intensity of some peaks observed on the ceramics X-rays diffraction diagram.[9,10]

For sintering temperatures more than 1500 °C and for times higher than 1 h, the open porosity of ceramics is lower or equal to 0.8%, whereas compactness is always above 92%.

With this material process, the material is dense enough for our applications and the porosity is mainly closed, that means that this refractory is well adapted for severe accidents conditions.

The image recorder with the scanning electron microscope (SEM) in Fig. 3 shows the microstructure of the HfO_2–Y_2O_3 (5 mol%) ceramic materials. This micrography has been taken with backscattered electron images: shades of grey in the image depend on the chemical elements present in the sample. The higher the atomic mass of the chemical element, the clearer the image. Fig. 3 shows a very specific microstructure, representative of a composite material with two phases: grey nodules of different size (5–15 μm) are dispersed inside a more clear grey matrix; these grey nodules are those containing most of the yttrium, i.e. the cubic solid solution Hf_x–$Y_{1-x}O_2$. The observation of the grey nodules shows that the cubic solid solution Hf_x–$Y_{1-x}O_2$ is present almost systematically around a pore. These pores have on average size of 3 μm, which corresponds to the size of the agglomerates of yttrium oxide observed with the laser granulometer.

The presence of the solid solution around the pores suggests a Kirkendall effect occurred during the sintering, i.e. the existence of a great difference between diffusion rates of the two cations (Y^{3+} and Hf^{4+}) in the solid solution. Fig. 4 schematizes the principle of the Kirkendall effect applied to HfO_2–Y_2O_3 ceramics. In fact, yttrium diffuses more quickly than hafnium in the solid solution: the place previously occupied by Y_2O_3 corresponds to a pore at the end of the sintering.

The X-rays diffraction diagrams of ceramics containing 3, 5 and 8 mol% of Y_2O_3 are presented in Fig. 5.

Porter and Heuer[9] highlighted (by taking account of the concept of factor of multiplicity and the linear absorption coefficient) that the volumetric fraction of the monoclinic phase in a zirconia stabilized by magnesia could be written as (I_m and I_c indicate the intensity of the monoclinic and cubic phase):

$$V_m = \frac{1.6031 I_m(1\,1\,-1)}{1.6031 I_m(1\,1\,-1) + I_c(1\,1\,1)}$$

By using this formula, it is possible to estimate the percentages of monoclinic and cubic phases inc ceramics materials because ZrO_2 physical properties are similar to HfO_2 ones. The results are shown in Table 4.

This table highlights that the cubic solid solution phase increases with the percentage of Y_2O_3.

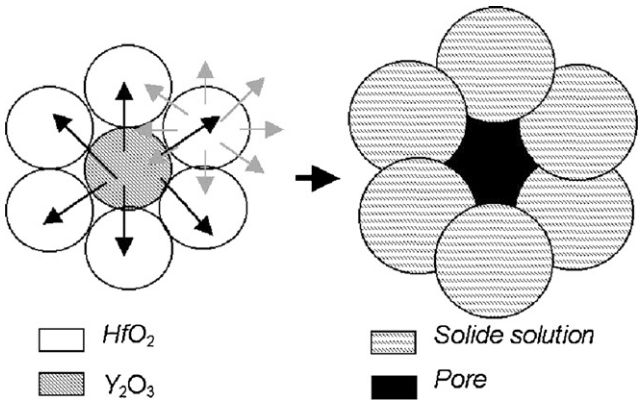

Fig. 4. Kirkendall effect and HfO_2–Y_2O_3 composite materials.

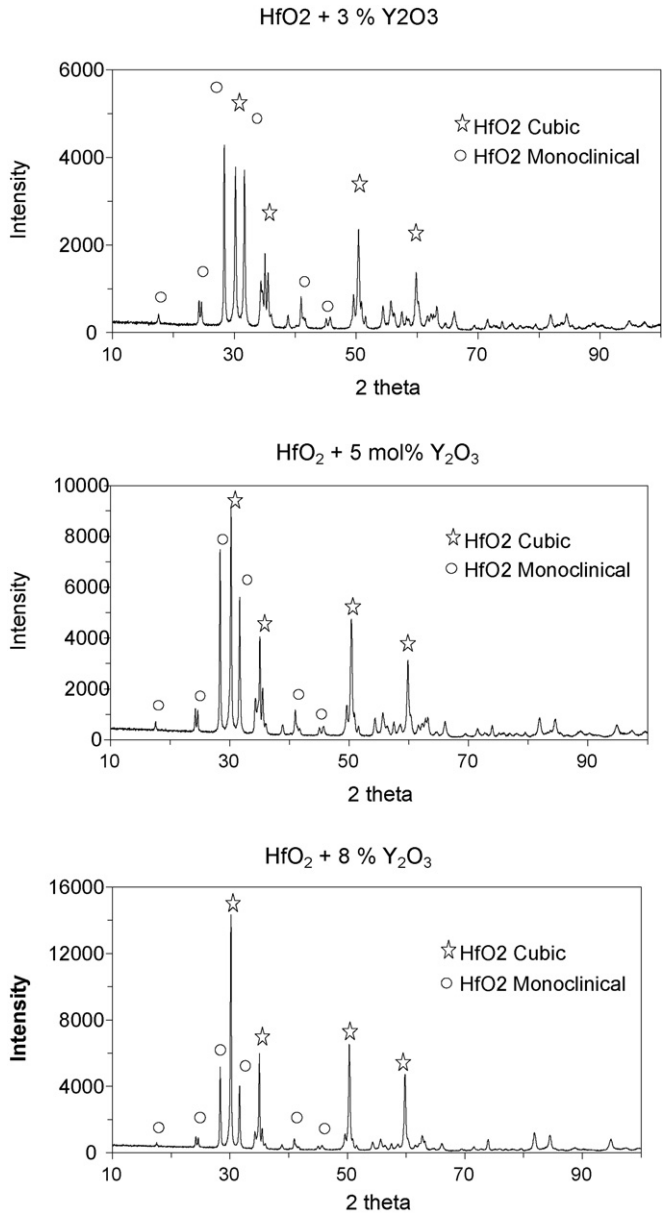

Fig. 5. X-rays diffraction diagrams of ceramics containing 3, 5 and 8 mol% of Y_2O_3.

4.2. Porous pieces

The porous pieces are obtained by elimination of organic elements during de-binding before sintering. This thermal treatment consists on the pyrolytic degradation of the organic materials at 600 °C.

Table 4
Phase distribution.

Composition	Monoclinic phase (%)	Cubic solid solution phase (%)
HfO_2 + 3 mol% Y_2O_3	61	39
HfO_2 + 5 mol% Y_2O_3	57	43
HfO_2 + 8 mol% Y_2O_3	37	63

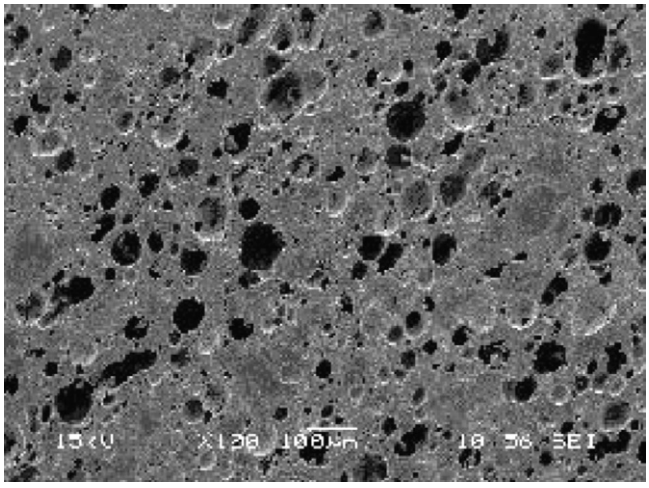

Fig. 6. Image of a HfO_2 and 70 vol% porous agent 1 sintered piece.

According to pore forming material, different de-binding cycles were tested.

The results are satisfactory only for porous agent 1, which allows obtaining no cracking with porous pieces. A microstructure of this porous ceramic with 70 vol% porous agent 1 is shown Fig. 6. This micrography highlights a very porous matrix. The final pores have a diameter ranging between 40 and 100 μm, whereas initial size of the porous agent is 85 μm. This shows that the porosity has been partially stabilized during sintering process. The quantity of porous agent does not correspond to porous volume because the porous agent is water-soluble and because the smallest porosity disappeared during sintering stage. It must be stressed that these materials have a good mechanical resistance in spite of their strong porosity.

The origin of cracks in the porous pieces containing the porous agent 2 can be induced by the difference of vitreous transition temperatures between agents 1 and 2. It is known that the Young's modulus decreases at the vitreous transition temperature. At room temperature, the porous agent 2 presents a higher Young's modulus than porous agent 1. The too high Young's modulus of porous agent 2 could cause problems of cracking during the pressing step (too high relaxation of the green body after pressing).

4.3. Characterization for VERDON: resistance to cracking

During VERDON tests, pieces will be submitted to temperatures up to 2600 °C.

It is important to know the behavior of the dense and porous pieces in the temperature range where the volumetric expansion occurs, i.e. between 1600 and 1800 °C. The ceramics obtained by using the reference process have been heated up to 1800 °C. The results are shown in Table 5.

The dense and porous pieces do not crack during the volumetric expansion, respectively due to both the stabilizing agent and the high rate of porosity. Tests were also carried out on hafnium dioxide not stabilized dense pieces, ceramics have then undergoes significant cracking.

Table 5
Ceramic characterization of phase transition resistance.

Composition	Type	Compacity (%)	Open porosity (%)	State after treatment at 1800 °C, 1/2 h
HfO_2	/	95.1	3.0	Fissuration
HfO_2 + 5 mol% Y_2O_3	Dense piece	88.3	0.4	Intact: no crack
HfO_2 + 8 mol% Y_2O_3	Dense piece	91.2	0.4	Intact: no crack
HfO_2 + 40 vol% porous agent 1	Porous piece	72	28	Intact: no crack
HfO_2 + 70 vol% porous agent 1	Porous piece	48	52	Intact: no crack

4.4. Characterization for VERDON: severe accident conditions

At CEA-Cadarache, an apparatus, called VITI (VIscosity Temperature Installation),[11] has been developed to perform high-temperature measurement, such as viscosity and surface tension measurements on corium by aerodynamic levitation within the experimental corium European platform PLINIUS.

To obtain high temperature up to 2600 °C, a radio frequency generator is coupled with the diffuser and the pressing membrane (both in graphite). The oxide sample is heated at low temperature by thermal radiation of the susceptor. At higher temperature directly (volumetric heating) with the electromagnetic field induced inside the oxide materials (the oxides are electric conductors at high temperature) and always indirectly with the thermal radiation (areal heating).

A bi-chromatic pyrometer ($\lambda_1 = 0.92\,\mu m$, $\lambda_2 = 1.04\,\mu m$) is used to measure the surface temperature of the droplet between 1300 and 2800 K. The video recording is set up with a numeric video tape recorder and a software allows the characterization of the materials.

Temperature cycles have been applied on hafnium dioxide pieces to qualify the temperature resistance. The hafnium dioxide pieces were not manufactured according to the final geometry of VERDON facility, but were under the form of pellets and in direct contact with the C-support. Tests have been conducted up to 2500 °C. However, at this temperature, diffusion at solid state is very rapid and some interactions have been observed between HfO_2 and C, forming Hf and HfC.

In future, it is planned to use tungsten susceptor and a hafnium dioxide tube like in VERDON facility to avoid direct contact between HfO_2 and the graphite heater.

4.5. Characterization for VERDON: thermal conductivity

The thermal conductivity of the porous pieces is a very significant parameter because these ceramics must play the role of thermal insulator.

The effective thermal conductivity of a porous material depends on many parameters: the thermal conductivity of the solid (i.e. conductivity of dense material, function of temperature), the proportion of air voids, and their distribution. In a porous material heat is propagated according to three processes: conductivity through the solid, and convection and radiation through the pores. It is necessary to know what is the critical size of the pores, i.e. the size which generates a brutal increase in the thermal conductivity of material.

A model has been developed which allows considering the thermal conductivity of zirconium dioxide at high temperature ($T > 2000$ K). The hafnium dioxide presents many similarities with the zirconium dioxide thus this model has been used to calculate the thermal conductivity of the hafnium dioxide at high temperature, as shown below:

$$\lambda = \left(\frac{1}{aT + b}\right) + cT^3 \tag{1}$$

$1/(aT+b)$ describes the transfer by vibration of the crystal lattice. The coefficients a and b are calculated starting from experimental values of thermal conductivity at low temperature ($T < 800$ K); cT^3 estimates the transfer by radiation at high temperature.

Values of hafnium dioxide thermal conductivity at low temperature have been published by Ferrero.[3] However, no indication has been found to calculate the transfer by radiation at high temperature for the hafnium dioxide thus the coefficient c has been assumed equal to that used for zirconium dioxide: $c = 1.3 \times 10^{-10}$.

According to this model, the thermal conductivity of dense hafnium dioxide can be determined between 300 and 2800 K by using the following formula:

$$\lambda = \frac{1}{(6.05 \times 10 - 5\,T + 0.589) + 1.3 \times 10^{-10} T^3} \tag{2}$$

A model of percolation, recently developed[12] makes it possible to calculate the thermal conductivity of a porous material, knowing the thermal conductivity of the dense material. This model assumes that the material can be divided in areas of phase 1 or 2 of similar sizes, one of the phase being the pores (air) and the material (dense):

$$\begin{aligned}\lambda_{porous} = 0.25[&\lambda_{air}(3V_{air} - 1) + \lambda_{dense}(3V_{dense} - 1) \\ &+ ([\lambda_{air}(3V_{air} - 1) + \lambda_{dense}(3V_{dense} - 1)]^2 \\ &+ 8\lambda_{air}\lambda_{dense})^{1/2}]\end{aligned} \tag{3}$$

with V_{dense} the volumetric fraction of material, V_{air} the volumetric fraction of pore and λ_{air} = function (T)

The model of percolation is valid for porosities ranging between 25% and 60%. This model allows calculation of porous hafnium dioxide thermal conductivity as a function of the temperature. The curves are presented Fig. 7. These curves highlight that hafnium dioxide thermal conductivity decreases with the proportion of air voids as expected since the air has a lower thermal conductivity than dense hafnium dioxide.

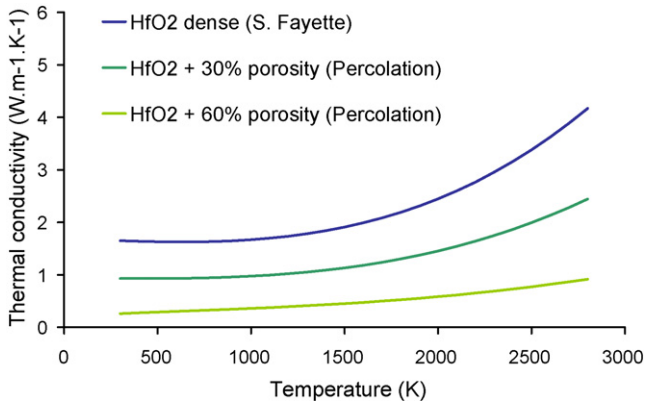

Fig. 7. Thermal conductivity of dense and porous HfO_2 material.

The model of Loeb[13] does not describe well thermal conductivity for a porous material, but it makes it possible to evaluate the influence of the radiation on thermal conductivity. This model assumes no-disturbance of the heat flux by the pores, but the conductivity of gas is not taken into account, it is valid for porosity lower than 30% (Eq. (4)):

$$\lambda_{\text{porous}} = \lambda_{\text{dense}} \left[\frac{(1 - P_c) + P_c}{[P_l \lambda_{\text{dense}} / 4\sigma\varepsilon\gamma d T^3] + 1 - P_l} \right] \quad (4)$$

with P_c the surface fraction of pore in the orthogonal plan of heat flow, P_l the linear fraction of pore in the direction of heat flow, σ the constant of Stefan Boltzmann, ε the emissivity of surfaces, γ a factor related to the form and d characteristic dimension of pores.

With this model it is possible to define the pore diameter for which the radiative contribution through the pores becomes dominating. This calculation was carried out for porous hafnium dioxide with 30%. The curves are presented in Fig. 8. The calculation highlights that the limit pores size at high temperature is 100 μm. For the insulating pieces of VERDON facility, the choice of the porous agent with a size diameter 85 μm does not generate significant increase in thermal conductivity at high temperature according to this modelling. So, it validates the use of the styrene butadiene copolymer as porous agent.

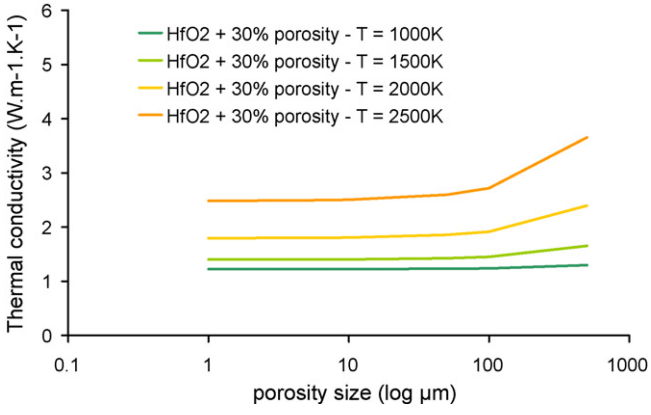

Fig. 8. Critical size of porosity.

5. Conclusion

The VERDON facility, devoted to the study of irradiated fuel behavior in case of PWR severe accident, and more particularly to the source term quantification (fission products (FP) and actinides release and transport), will be available mid-2008 at CEA Cadarache. The fuel sample will be heated in an inductive furnace under controlled atmosphere simulating the conditions of a hypothetical severe accident. FP release kinetics will be measured on line.

In this installation, refractory materials must be used and will be submitted to severe accidents conditions: 2600 °C, steam, hydrogen, air and for some refractory pieces interactions with corium. For this installation, new refractory materials are needed. In this context the CEA has evaluated different solutions and has chosen to evaluate the hafnium dioxide refractory materials, well known to resist at high temperature and especially to chemical interactions. Nevertheless, no industrial refractory hafnium dioxide materials answering to VERDON needs were available. For this reason, a specific process has been developed to manufacture porous and dense hafnium dioxide materials for VERDON facility. Yttrium oxide has been chosen as stabilizing agent of the high-temperature phase for dense material and a polymer for porous materials. All VERDON pieces (dense and porous) are realized by semi-isostatic pressing. The dense pieces (HfO_2 + 3–8 mol% Y_2O_3) present a density about 92% but a closed porosity, which is in agreement with the VERDON conditions. For porous pieces, different porous agents were tested. The PSB porous agent only avoids cracking of sintered pieces. The thermal conductivity of porous piece is also in agreement with the VERDON conditions. Qualification at intermediate temperature has been successfully realized and it is planned to realize qualification up to 2600 °C in the next months. At least, the specific geometry of VERDON facility needs an adaptation of the process currently under development.

Acknowledgement

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References

1. Pontillon, Y., Malgouyres, P. P., Ducros, G., Nicaise, G., Dubourg, R., Kissane, M. *et al.*, Lessons learnt from VERCORS tests: study of the active role played by UO_2–ZrO_2–FP interactions on irradiated fuel collapse temperature. *Journal of Nuclear Materials*, 2005, **344**(1–3 (September)), 265–273.
2. Clément, B., Hanniet-girault, N., Repetto, G., Jacquemain, D., Jones, A. V., Kissane, M. P. *et al.*, LWR severe accident simulation: synthesis of the results and interpretation of the first Phebus FP experiment FPT0. *Nuclear Engineering and Design*, 2003, **226**, 5–82.
3. Ferrero, G. L., Propriétés d'oxydes réfractaires simples, EUR 4756 f, 1972.
4. Curtis, C. E., Doney, L. M. and Johnson, J. K., Some proporties of hafnium oxyde, hafnium silicate, calcium hafnate and hafnium carbite. *Journal of American Ceramic Society*, 1956, **39**(10), 458–465.
5. Blanc, P., Elaboration et caractérisation de membrane d'ultrafiltration et de nano-filtration en hafnie, Ph.D. Thesis, Université de Montpellier, France, 1995.
6. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. John Wiley, 1975.

7. Levin, E. and Mcmurdie, H., *Phase Diagram for Ceramists*, 1975, **3**.
8. Chartier, T., Delhomme, E., *Mécanique et Ingénierie des Matériaux*, Matériaux et Processus Céramiques. Hermès Science Publications, 2001, pp. 141–217.
9. Porter, D. L. and Heuer, A. H., Microstructural development in MgO partially stabilized zirconia. *Journal of American Ceramic Society*, 1979, **62**(5–6), 298–305.
10. Isupova, N., Glushkova, V. B. and Keler, E. K., The HfO_2–Y_2O_3 system in the region rich in hafnium dioxyde. *Inorganic Material*, 1969, **11**(5), 1658–1661.
11. Piluso, P., Monerris, J., Journeau, C. and Cognet, G., Viscosity measurements of ceramic oxides by aerodynamic levitation. *International Journal of Thermophysics*, 2002.
12. Piluso, P., Fayette, F., Etude des propriétés thermiques du corium - Base de données CORPRO, *Matériaux 2002 - session modélisation des matériaux hétérogènes*, Tours, France, 2002.
13. Loeb, A. L., Thermal conductivity: a theory of thermal conductivity of porous materials. *Journal of American Ceramic Society*, 1954, **37**(2), 96–99.