

# Thermophysical characterization of nitrides inert matrices: Preliminary results on zirconium nitride

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## Abstract

Preliminary results have been obtained on a research program confirming the attainment of reliable procedures to perform property measurements on nitride fuels. The thermal transport properties of ZrN were measured; the results obtained so far confirm or extend the range of data available in literature. Increasing trends with temperature were observed, in line with predictions. These activities will be extended to nitride fuels and to systems containing Pu and other actinides like UN, (U<sub>x</sub>Pu<sub>1-x</sub>)N, (Zr<sub>0.8</sub>Pu<sub>0.2</sub>)N, and irradiated nitride samples.

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## 1. Introduction

In the context of the initiatives to ensure sustainable energy supplies to satisfy future demands, several international programs (such as Generation IV) are considering advanced nuclear reactors and nuclear fuel cycles. Nitride and carbide compounds enjoy renewed interest worldwide as possible nuclear fuels for high temperature gas cooled reactors [1], for liquid metal fast breeder reactors and also for space power reactors [2].

The research and development programs on nitride fuels for fast breeder reactors were pursued in USA, France, Germany, United Kingdom, Russia, Japan and India during 1960s and 1970s. They had been identified as primary advanced nuclear fuels, because of their high heavy metal density, high thermal conductivity and excellent com-

patibility with sodium coolant [1,3,4]. With the expansion of LWR and related oxide fuel systems, and later under the effects of the crisis that hit nuclear energy, essentially all research activities on nitrides as nuclear fuel for electricity production were abandoned during the subsequent decades.

At present, there is an effort to regain a full experimental maturity on these types of non-oxide fuel systems [5–9]. This effort will be required to establish a reliable and comprehensive base of data that allows updating and/or developing the necessary modeling tools to predict the operational behaviour of advanced fuels.

Zirconium nitride is considered as an inert matrix for burning plutonium in a closed nuclear fuel cycle [10]. Having the fissile material diluted in a matrix would soften the high fission density and consequently reduce the maximum fuel temperatures that would be reached in pure PuN and PuO<sub>2</sub> in a fast neutron spectrum. The ZrN is foreseen to be used as either homogeneous or

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heterogeneous diluent for Pu, because of its chemical and thermodynamic compatibility with the actinide (and also with the liquid metal coolant). An additional advantage of nitrides is their good reprocessing behaviour (easy to dissolve in nitric acid). The characterization of thermophysical properties plays a key role in assessing performance and safety aspects related to the in-pile behaviour of nitride fuel systems. Recent work by Basini et al. [6] provided new experimental data concerning thermophysical properties of zirconium nitride.

In the Institute for Transuranium Elements (ITU), a joint research centre of the European commission, design and interpretation of experiments, along with characterization of both fresh and irradiated nitride fuels have been resumed [5]. Both physical and chemical phenomenological modeling and experimental activities are included in this effort.

This paper presents an overview of experimental results obtained from the first investigation campaigns on ZrN. These data constitute the first part of a larger program of characterization, which will include studies on UN, on solid solutions (U, Pu)N and (Zr, Pu)N and on irradiated nitride fuel samples [5,7].

## 2. Experimental

### 2.1. Materials

Zirconium nitride pellets were sintered from powder (Alfa Aesar) with 87.53 wt% zirconium and 12.29 wt% nitrogen corresponding to the formula  $ZrN_{0.9088}$ , in agreement with the presence of a homogeneous nitrogen low-content region in the zirconium nitride phase diagram [11]. The main impurities were hafnium (0.6739 wt%), and carbon (0.09 wt%).

The ZrN samples were carbo-thermally reduced into sintered cylindrical pellets. Pellet fabrication was performed at ITU. The pellets had a density (measured with the Archimedes's immersion method) of 82.4% of the theoretical value. The density measured with the geometrical method was 80.6%. This indicates, according to the formula reported on the European standard EN-623-2:1993D, that there is  $\sim 10.2\%$  of open porosity over the 19.4% porosity for the ZrN samples.

The open porosity has no effect on the specific heat analysis, where only the total mass is significant. However, it is very important for the measurement of the thermal diffusivity and for the

determination of the thermal conductivity. The contribution to the thermal transport by the porosity,  $K_{\text{pore}}$  (where also the shape of pores can be relevant) must be factored in. In this case the porosity contribution to the thermal conductivity of the sample was taken into account using the factor  $\beta$  in the Maxwell–Eucken equation [18].

### 2.2. Techniques

The specific heat was measured using a differential scanning calorimeter (DSC), (Netzsch STA-409). This device is located in a glove box to be able to characterize radioactive materials; the temperature calibration was made with the melting point determination of Sn, Zn, Al, Ag and Au; the gas atmosphere during the tests was ultrapure Argon6.0 (gas impurities  $< 1$  ppm) with a flux  $\varphi = 100$  ml/min; oxygen filters were placed on the gas line prior to entering the DSC oven.

Thermal diffusivity measurements (hence, knowing density and specific heat, thermal conductivity determinations) were carried out using a Laserflash apparatus (LAF) developed in ITU [12]. The device is placed in a Pb-shielded glove box equipped with remote manipulators, and is designed to perform measurements on irradiated fuel samples up to very high burnup levels. Before the LAF tests, the emissivity values of ZrN were measured using a black cavity radiation integrating sphere. The emissivity mean value was  $\varepsilon = 0.9018$  at  $\lambda = 1060$  nm and  $T = 300$  K, see for comparison [13].

Structural and phase characterization of the samples was performed using SEM, TEM, and XRD. In parallel with the thermophysical property measurements, a study of the oxidation process was initiated: thermogravimetry (TG), which allows determining critical temperature levels for oxidation, was combined with microstructural examination using SEM and ceramography phase analysis by optical microscopy.

### 2.3. Optimization of experimental approach

The first stage of the research plan was focused on the adaptation of existing experimental facilities, until now applied mainly to study oxide fuels, to oxidation-sensitive compounds. The necessity to adapt the facilities to minimize oxidation and other possible reactions became evident in particular for the high temperature measurements. Several methods to limit unwanted reactions were tested.

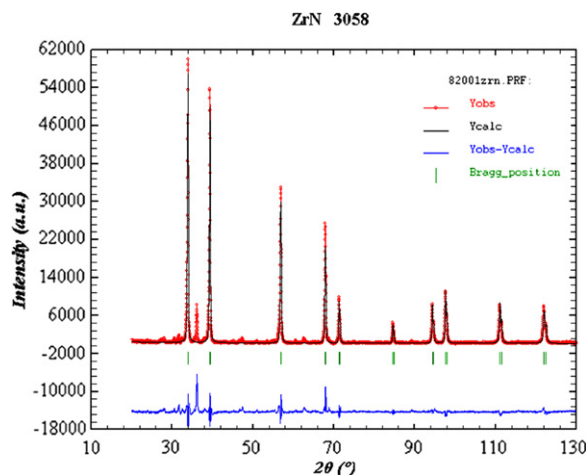


Fig. 1. XRD spectra of the as-sintered ZrN sample. Red line: measured spectrum; black line: pure nitride spectrum; blue line: oxide phase, obtained by subtracting the black from the red line. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Different solutions were then adopted for different measurement techniques. Oxygen traps were mounted on the gas line supplying the DSC furnace. In the case of the LAF, good results were obtained by applying a thin coating of graphite onto the surface of the sample.

The oxidation behaviour of ZrN was characterized also by thermogravimetry: a value for the critical temperature  $T_c \sim 550$  °C was determined in air at 1 bar, with a flux  $\varphi = 10$  ml/min. This  $T_c$  value falls within the range of values reported by Caillet et al. [14] (obtained at oxygen pressure values in the range 0.066 and 0.66 bar).

Fig. 1 shows the XRD diagram for the as-sintered ZrN, obtained with Cu-K $\alpha$  radiation, on a milled ZrN sample. The lattice parameter obtained from these measurements was  $a = 4.57665$  Å, in substantial agreement with the reported value of  $a = 4.575$  Å [11]; the higher lattice parameter value of our sample was probably due to the presence of carbon and oxygen impurities.

The measured peaks intensity shown in Fig. 1 (red line)<sup>1</sup> is higher than the expected ZrN peaks intensity (black line) at  $2\theta = 32^\circ, 34^\circ, 54^\circ, 68^\circ$ , etc., indicating the presence of a ZrO<sub>2</sub> phase (blue line). This was confirmed using a CO infrared detector with a sensitivity of 0.01  $\mu\text{g}$  and an accuracy of  $\pm 0.2\%$ : the measured oxygen concentration was  $\sim 0.9$  wt%.

<sup>1</sup> “For interpretation of color in this figure the reader is referred to the web version of this article”.

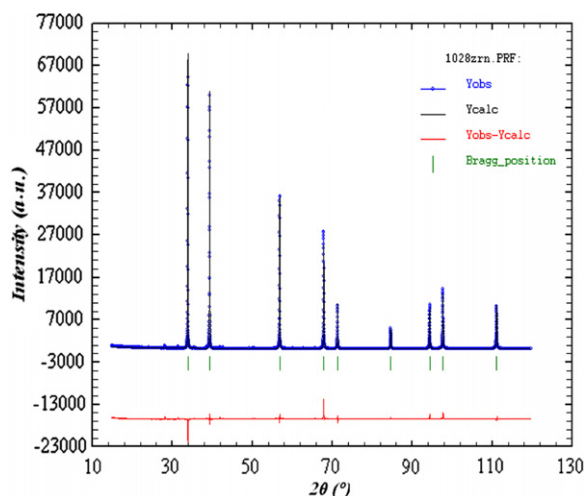


Fig. 2. XRD spectra after sample treatment to remove the oxide phase from the surface. Essentially no oxide phase is detected. Blue line: measured spectrum; black line: pure nitride; red line: oxide phase (black line subtracted from blue line). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

The oxide phase was mainly located on the surface. This was confirmed by the fact that an XRD spectrum taken after adopting a sample treatment procedure affecting mainly the surface, as shown in Fig. 2, showed no oxide peaks. This indicated that the amount of oxide phase was below the detection limit ( $\sim 3$  vol.%). The preparation procedure to minimize oxygen content in the ZrN samples consisted of alternating ultrasonic cleaning in baths of acetone with cold grinding of the surface; a thermal treatment at 200 °C for 2 h in ultra-pure Argon 6.0 atm completed the process.

The characterization of this type of sample will be extended to surface analysis by Raman spectroscopy, (in collaboration with the Nuclear Engineering Dept. of Politecnico of Milan) in order to study the ZrO<sub>2</sub>–ZrN interface and phase distribution on the surface.

### 3. Results and discussion

#### 3.1. Specific heat

Fig. 3 shows the results of  $C_p$  measurements on ZrN disks using the DSC. The experimental data (average of four runs) are interpolated by the following curve:

$$C_p [\text{J/mol K}] = 43.5 + 6.82 \times 10^{-3} T - 6 \times 10^5 T^{-2} \quad (1)$$

for  $373 \text{ K} < T < 1463 \text{ K}$ .

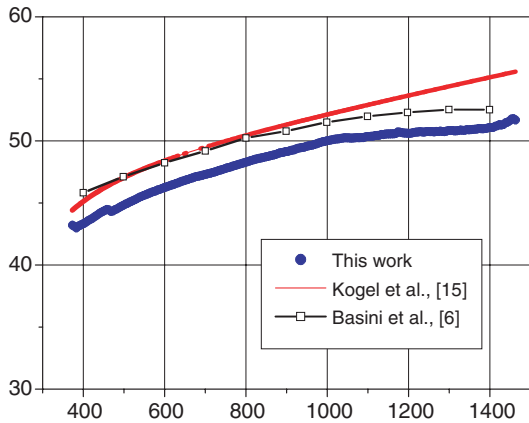


Fig. 3. Specific heat of ZrN measured by DSC. Average of four ascending/descending temperature cycles (blue line). Experimental results from [6] and a theoretical curve from [15] are also reported for comparison. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Eq. (1) has an average error of 1.15% compared with the experimental data. At high temperature, the experimental data slightly diverge from the fitting equation (with a maximum error  $\sim 4\%$ ). It is not clear at this stage if this behaviour represents a limitation of the measurement technique or if it is related to high temperature reactions occurring in the sample. This high temperature behaviour will be the object of further investigation. It must be noted, though, that the ZrN samples appeared darker after a few measurement cycles, which would indicate the occurrence of a high temperature reaction during the DSC runs. The discontinuity observed around 470 K is an artifact of the measurement, probably connected with heat and electrical transport disturbances at the DSC thermocouple and/or at the temperature controller. The present  $C_p$  correlation matches very closely the trend of the theoretical curve by Kogel et al. [15] as reported in [6] (in the original paper by Kogel [15] the correlation is reported only graphically, without indication of its numerical expression), with a difference  $< 5\%$  by comparing the numerical values. These data are also in good agreement with the experimental values from [6]. In [15] a theoretical calculation is made, by assuming that thermal vibrations of the lattice occur along a line of M–X–M bonds. From IR spectra on ZrN powder (0.2 wt% of oxygen impurity), the Einstein characteristic temperature  $\theta_E = 1584$  K, and the generalized Debye characteristic temperature  $\theta_D = 645$  K were obtained. This calculation predicts the occurrence of increasing  $C_p$

trends in the temperature range corresponding to the present measurements. In this work, an increasing (referred to  $\theta_E$ ) Einstein-like specific heat curve was obtained in the experimental range  $373$  K  $< T < 1463$  K, in good agreement with [15].

### 3.2. Thermal diffusivity and thermal conductivity

Fig. 4 shows the results of thermal diffusivity measurements by LAF on graphite-coated ZrN disks. The following curve was obtained:

$$\alpha \text{ [m}^2\text{/s]} = 2 \times 10^{-9} T \text{ (K)} + 3 \times 10^{-6} \quad (2)$$

for  $520$  K  $< T < 1470$  K. The estimated error was  $\sim 4\%$ .

There is no accepted reference curve for the temperature dependence of thermal diffusivity of ZrN. Basini et al. [6] report an almost constant or slightly decreasing value of  $\alpha \sim 7 \times 10^{-6}$  m<sup>2</sup>/s with increasing temperature over a broad temperature range. The results obtained in this work (see Fig. 5) indi-

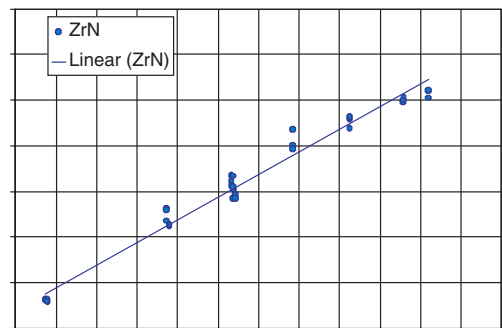


Fig. 4. Thermal diffusivity of ZrN measured by laserflash. Sample coated with graphite.

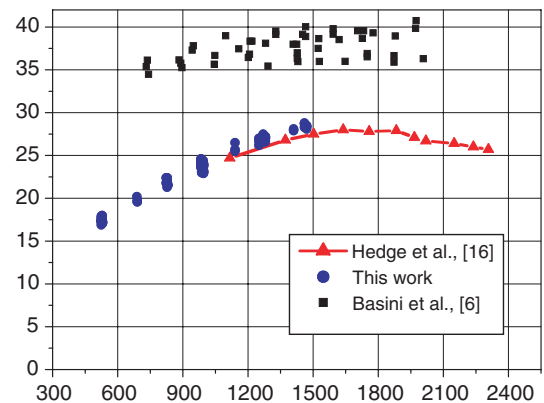


Fig. 5. Thermal conductivity of ZrN. Sample coated with graphite. All data in the figure are corrected to 100% density.

Table 1  
Density of the ZrN samples

Method	Measured density (g cm <sup>-3</sup> )	Theoretical density (g cm <sup>-3</sup> )
Geometrical	5.87 ± 0.1	7.29
Immersion	6.00 ± 0.3	7.29

cate an increasing trend for thermal diffusivity *vs.* temperature, in agreement with Hedge et al. [16]. It seems more likely to have an increasing thermal diffusivity with increasing temperature, mainly because of the broad band on both sides of the Fermi level for ZrN, which causes the metallic behaviour, and is primarily due to the metal d orbitals, as calculated in Bazhanov et al. [17].

Fig. 5 shows the thermal conductivity  $\lambda$  as a function of temperature for the ZrN samples calculated as

$$\lambda = \alpha\rho C_p, \quad (3)$$

where  $\rho$  is the density, as determined by the Archimedes method. The data correspond to three measurement runs, and are shown together with those from Refs. [6,16]. For proper comparison, all data on the figure are corrected to 100% of the theoretical density. As mentioned earlier for thermal diffusivity, there is a very good agreement between our results and those by Hedge et al. [16], while the values from [6] appear much higher.

Actually the main difference between our samples and those from [6] is the density, ~80.6% TD and 70% TD, respectively. Unfortunately, no details about the samples fabrication are given in [6]. The conclusion is that the data reported here are considered reliable with regard to the thermal conductivity and diffusivity of ZrN, because in good agreement with the literature data by Hedge [16], which refer to hot pressed (2373.2 K) ZrN samples with a density ~89.16% TD, measured in the temperature range 1117 K <  $T$  < 2308 K (See Table 1).

#### 4. Conclusions

The results obtained in this first stage of the research program confirming the attainment of reliable procedures to perform property measurements on nitride fuels. The thermal transport properties of ZrN were measured; the results obtained so far confirm or extend the range of data available in literature. Increasing trends with temperature were observed, in line with predictions. These activities will be extended to nitride fuels and to systems

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