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Experimental assessment of thermophysical properties of (Pu, Zr)N

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Abstract

The thermophysical properties of plutonium–zirconium nitride (0–25 at.% Pu), namely heat capacity, thermal conductivity and thermal expansion were measured on pellets produced thanks to the well established pellet pressing route. The experimental results obtained on ZrN were consistent with the existing literature data. The thermal properties measurements reported for $(Pu_{0.25}Zr_{0.75})N$ were in rather good agreement with predictive values calculated from ZrN and PuN available data.

1. Introduction

Implementation of accelerator driven systems (ADS) for the purpose of burning americium and degraded plutonium may enable a significant reduction of the radio-toxic inventories directed to geological repository. The properties of ADS fuels must allow irradiation up to high burnup without degradation of safety margins or reprocessability. Nitride fuels are interesting in this context.

In order to predict the in pile behaviour of nitride fuels, many thermophysical properties have to be assessed. The most important properties involved in the prediction of the fuel temperatures are heat capacity, thermal expansion, and thermal conductivity. So, a characterization program has been carried out to evaluate these properties on zirconium nitride and plutonium–zirconium nitride solid solution (Pu/Zr + Pu = 25 at.%), from samples elaborated thanks to the well established pellet pressing route.

The measurements reported here on ZrN and (Pu, Zr)N were compared with calculated values and literature data.

2. Experimental

The thermal diffusivity was measured by a laser flash technique. A laser pulse (energy: 40 J, duration: 1 ms, wavelength: 1 μm) was directed on the front face of a sample (1 mm thick disk) located inside a high frequency induction furnace under argon atmosphere. The laser pulse was absorbed at the surface of the disk. An infrared detector was used to measure the temperature from the rear face of the sample over the range 700–2000 K. An opaque coating (thin layer of carbon) was needed

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on the front face of the specimen to overcome the problem of transparency of the zirconium nitride based materials to laser radiation and also to ensure uniform absorption of the laser pulse energy by the sample. The variations of the rear face temperature as a function of time were analyzed by a method taking into account radiation and convection losses. The thermal diffusivity was then calculated by minimizing the difference between a calculated thermogram and the experimental one.

The thermal conductivity was obtained as the product of the experimentally measured thermal diffusivity, heat capacity, and density, according to the relationship:

$$K = D\rho C_p,$$

where K is the thermal conductivity (W m^{-1} K^{-1}), D is the thermal diffusivity (m^2 s^{-1}), ρ is the density (kg m^{-3}), and C_p is the heat capacity (J kg^{-1} K^{-1}). The effect of porosity was separately calculated. The measurement of the bulk density of the samples was carried out by a liquid immersion technique under vacuum using bromobenzene as the immersion liquid. To calculate the density in temperature the linear thermal expansion coefficient data ($\Delta L/L_0$) were determined experimentally from a SETARAM TMA 92 dilatometer. Density was then calculated versus temperature as $\rho = \rho_0/(1+\Delta L/L_0)^3$ where the subscript 0 refer to the room temperature values. A differential scanning microcalorimeter (DSC 404 NETZSCH) was used for heat capacity measurements up to 1400 K.

The uncertainties were estimated to be about 5% for the thermal diffusivity, 5% for the heat capacity, and 1% for the density. Hence the precision on the absolute values of the thermal conductivity was estimated at about 11%.

3. Results and discussion

Bulk densities of zirconium nitride and plutonium–zirconium nitride reported in Table 1 were found to be 5.10 and 8.31 g cm^{-3} respectively, and these densities correspond to 70% and 89% theoretical, respectively.

The TD were calculated by the X-ray method from the lattice parameter reported by Baker [1] for ZrN, and from the lattice parameter given by the Vegards law for (Zr, Pu)N as shown by Arai et al. [2] from the PuN parameter reported by Wriedt [3]. The values that can be found in literature for the TD of ZrN vary between 6.8 and 7.4 g cm^{-3} depending upon the determination method, the purity and the stochiometry (N/Zr ratio) of the material.

Table 1
Composition and density of the samples

Sample	Amount of PuN (mol%)	Bulk density (g cm^{-3})	Theoretical density (g cm^{-3})
ZrN	0	5.10 ± 0.05	7.29
(Pu, Zr)N	25	8.31 ± 0.08	9.34

3.1. ZrN

The dependence on temperature of the heat capacity of ZrN is shown in Fig. 1. It is seen that the heat capacity of zirconium nitride increases gradually as the temperature increases. Compared to the available literature data, the present measurements are in good agreement with the results reported in the Touloukian book [4] from Coughlin et al. and Hedge et al. measurements. In addition, the correlation given by Kogel et al. [5] predicts slightly lower values than the SGTE correlation [6] recommended by AEA-T/Harwell at temperatures above 500 K, but both generally predict fairly consistently with each other. The experimental results presented in this work were also consistent with these two correlations. The best fit (<5%) was obtained with the Kogel et al. correlation which was adopted here.

$$C_p(\mathrm{ZrN}) = 45.86 + 6.82\times10^{-3}\ (\mathrm{T/K}) - 5.54\times10^{5}\ (\mathrm{T/K})^{-2}\ [\mathrm{J\ mol^{-1}\ K^{-1}}].$$

The linear thermal expansion coefficient data used to calculate the dependence on temperature of density were given by the correlation recommended by Thetford and Mignanelli [16]:

$$\Delta L/L_0(\mathrm{ZrN}) = -0.0017 + 5.27\times10^{-6}\ (\mathrm{T/K}) + 1.15\times10^{-9}\ (\mathrm{T/K})^2.$$

The thermal diffusivity measurements on zirconium nitride, reported in Fig. 2, showed a small scatter of the data points for two different specimens and successive runs. No real trend can be observed in temperature, the thermal diffusivity remaining close to 7×10^{-6} m^2 s^{-1}. This result was consistent with the values obtained by Hedge et al. [7] and reported in the Touloukian book [8] in the range 1100–2300 K.

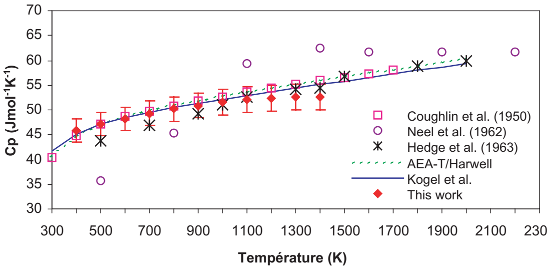

Fig. 1. Temperature dependence of heat capacity of zirconium nitride.

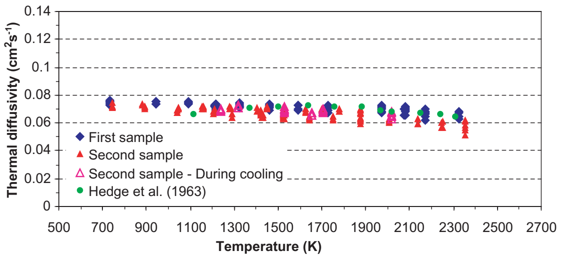

Fig. 2. Temperature dependence of thermal diffusivity of zirconium nitride.

Fig. 3 shows the dependence of the thermal conductivity on temperature. Between 700 and 2300 K the values obtained in the present work were located in the range 15–20 W m^{-1} K^{-1} and seemed to remain constant within the experimental error. The thermal conductivity data of zirconium nitride that can be found in literature [7,9,10], referenced in the Touloukian book [11] and also plotted in Fig. 3, were sparse and no reproductive, the most reliable being probably those from Hedge et al. [7], recently recommended by Kleykamp [12]. A comparison between the present results and the Hedge et al. data was made after correction to fully-dense materials using the modified Maxwell–Eucken correlation:

$$K_{\mathrm{TD}} = K/((1-p)/(1+\beta p)),$$

where K_{TD} is the thermal conductivity of the matrix with 100% theoretical density, and p the porosity fraction of the material. β is a coefficient ($0.5 \leqslant \beta \leqslant 3$) used to correct the characteristics of pores, the more closed pores, the higher the value. It was calculated, considering here β close to 1.7 due to a large fraction of open porosity, that the present corrected data were located in the range 35–40 W m^{-1} K^{-1} between 700 and 2300 K, and were systematically higher than the Hedge et al. corrected data for all temperature regimes. However the difference remained inside the range of error above 1200 K. The present corrected data can have been fitted to the following correlation:

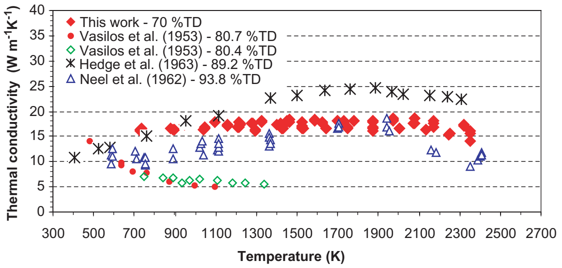

Fig. 3. Temperature dependence of thermal conductivity of zirconium nitride.

$$K_{\mathrm{TD}}(\mathrm{ZrN}) = 28.3 + 1.2 \times 10^{-2}\ (\mathrm{T/K}) - 3.7 \times 10^{-6}\ (\mathrm{T/K})^2\ [\mathrm{W\ m^{-1}\ K^{-1}}].$$

3.2. (Pu, Zr)N

The heat capacity of (Pu, Zr)N (25 mol% PuN) is shown in Fig. 4. It is seen that the heat capacity of plutonium–zirconium nitride increases gradually as the temperature increases, like previously observed on pure zirconium nitride. The same trend was also reported by Kubaschewski et al. [13] and by Oetting [14] for pure plutonium nitride. The data from Kubaschewski et al. and from Oetting were almost identical. Matsui [15] critically reviewed the heat capacity data of PuN and argued that the Oetting correlation was most reliable. Moreover Oetting correlation was recently recommended by Thetford and Mignanelli [16] and was also adopted here:

$$C_p(\mathrm{PuN}) = 45.002 + 1.542 \times 10^{-2}\ (\mathrm{T/K})\ [\mathrm{J\ mol^{-1}\ K^{-1}}].$$

The experimental heat capacity of plutonium–zirconium nitride solid solution had never been reported so far. Hence the present measurements were compared with estimated values only, calculated from ZrN and PuN available data according to the linear mixing rule:

$$C_p((\mathrm{Pu,Zr})\mathrm{N}) = xC_p(\mathrm{PuN}) + (1-x)C_p(\mathrm{ZrN}),$$

where x is the molecular fraction of PuN in the solid solution (here $x = 0.25$). C_p(PuN) and C_p(ZrN) refer to the heat capacity correlations from Oetting [14] and Kogel et al. [5] adopted here.

The heat capacity data from the present experimental work were slightly higher than the values predicted by calculation and also plotted in Fig. 4. The difference was around 10% at low temperatures, but remained inside the experimental uncertainty range (5%) between 800 K and 1400 K. The experimental data can have been fitted by the following correlation:

$$C_p((\mathrm{Pu_{0.25},Zr_{0.75}})\mathrm{N}) = 47.24 + 1.18 \times 10^{-2}\ (\mathrm{T/K}) - 2.78 \times 10^{-6}\ (\mathrm{T/K})^2\ [\mathrm{J\ mol^{-1}\ K^{-1}}].$$

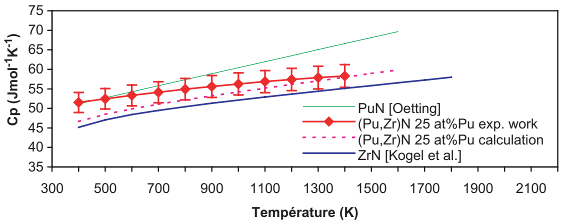

Fig. 4. Temperature dependence of heat capacity of $(\mathrm{Pu_{0.25}, Zr_{0.75}})$N.

The thermal expansion of plutonium–zirconium nitride is plotted in Fig. 5. The experimental results showed that the variation of the thermal expansion of $(Pu_{0.25}, Zr_{0.75})N$ versus temperature was quasi-linear up to 1800 K, leading to a constant value of the linear thermal expansion coefficient of about $8.7\text{–}8.8 \times 10^{-6}\ K^{-1}$. It is seen in Fig. 5 that the present measurements were in good agreement with the values calculated from PuN and ZrN available data according to the following mixing law:

$$\begin{aligned}&\Delta L/L_0((Pu_x, Zr_{(1-x)})N)\\&\quad = v\Delta L/L_0\ (PuN) + (1 - v)\Delta L/L_0\ (ZrN),\end{aligned}$$

where v is the volume fraction of PuN in the solid solution, converted from the molecular fraction of PuN x, the density ρ, and the molecular weight M, according to the relationship:

$$\begin{aligned}v &= \rho(ZrN) \cdot M(PuN) \cdot x/(\rho(PuN) \cdot M(ZrN)\\&\quad - (\rho(PuN) \cdot M(ZrN) - \rho(ZrN) \cdot M(PuN)) \cdot x),\end{aligned}$$

$\Delta L/L_0$ (ZrN) is the linear thermal expansion recommended by Thetford and Mignanelli [16] and $\Delta L/L_0$ (PuN) refers to the correlation suggested in the Touloukian book [17] and valid up to 1300 K:

$$\begin{aligned}\Delta L/L_0(PuN) &= -0.00342 + 1.154 \times 10^{-5}\ (T/K)\\&\quad + 5.561 \times 10^{-10}\ (T/K)^2\\&\quad - 1.205 \times 10^{-13}\ (T/K)^3.\end{aligned}$$

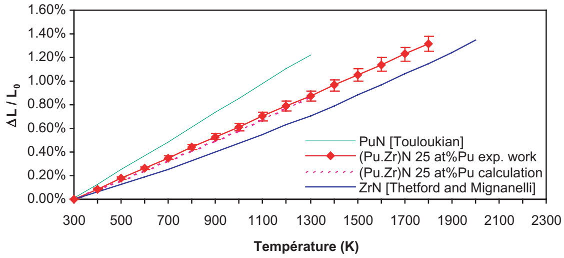

Fig. 5. Temperature dependence of thermal expansion of $(Pu_{0.25}, Zr_{0.75})N$.

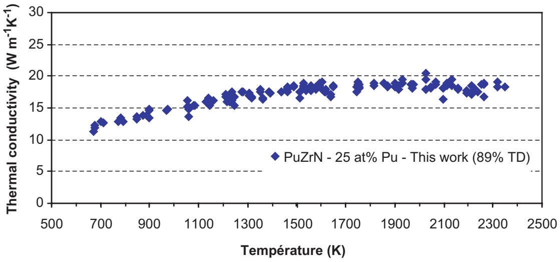

Fig. 6. Temperature dependence of thermal conductivity of $(Pu_{0.25}, Zr_{0.75})N$.

A maximum dispersion of about 10% around the mean values was observed on the experimental thermal diffusivity measurements, for all the temperature regimes. The corresponding thermal conductivity of (Pu, Zr)N (25 mol% PuN) is plotted in Fig. 6. It is shown that the temperature dependence of the thermal conductivity of plutonium–zirconium nitride was fairly modelled by a parabolic curve, reaching a maximum value of about $19\ W\ m^{-1}\ K^{-1}$ between 1600 and 2000 K. A similar trend was previously observed by Arai et al. [18] for pure plutonium nitride, with a maximum value of about $14\ W\ m^{-1}\ K^{-1}$ (data corrected to 100% TD).

The thermal conductivity of plutonium–zirconium nitride solid solutions had never been reported so far from experimentation. Hence the present measurements were compared with calculated values only. Fig. 7 shows that all the present experimental data, corrected to fully-dense materials with the modified Maxwell–Eucken correlation mentioned above ($\beta = 2$), were located within a channel delimited by two calculated correlations. It is

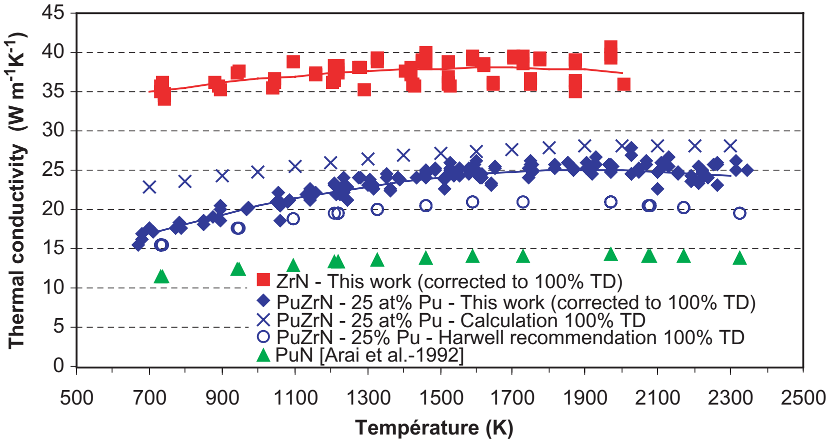

Fig. 7. Temperature dependence of thermal conductivity of ZrN and $(Pu_{0.25}, Zr_{0.75})N$. Data corrected to 100% TD.

seen that the present corrected data were systematically about 20% higher than the values predicted by the Harwell recommendation [16] (based on (U, Pu)N data), and approximately 15% lower than the values calculated from the model developed at ANL for Zr–U metallic alloys [19], extended to Zr–Pu binary alloys, and roughly applied here with the ZrN present data and PuN available data from Arai et al. The best fit of experimental data was given by the following correlation:

$$K_{\mathrm{TD}}((\mathrm{Pu}_{0.25},\mathrm{Zr}_{0.75})\mathrm{N}) = 4.801 + 2.11\times10^{-2}\ (\mathrm{T/K}) - 5.5\times10^{-6}\ (\mathrm{T/K})^2 [\mathrm{W\ m^{-1}\ K^{-1}}].$$

4. Conclusion

The most important thermophysical properties of plutonium–zirconium nitride (0–25 at.% Pu) involved in the prediction of the in pile fuel temperature, namely heat capacity, thermal conductivity, and thermal expansion, have been measured. The (Pu, Zr)N pellets used for the present characterization program were produced with a geometrical density of about 89 %TD.

It is shown that the experimental results obtained on ZrN were consistent with literature data. Furthermore, the thermal properties measurements reported here for $(\mathrm{Pu}_{0.25},\mathrm{Zr}_{0.75})\mathrm{N}$ were in rather good agreement with the predictive values calculated from ZrN and PuN available data.

Acknowledgements

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