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Experimental Investigations of Additives on the thermal conductivity UO_2 Pellets

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1. Introduction

The UO_2 conventional fuel used in PWR reactors is not a good conductor of heat, which generates an elevated temperature gradient in the UO_2 pellets, leading to premature fuel degradation. The thermal conductivity of UO_2 depends on microstructural parameters (e.g.: porosity and grain size) and atom-scale parameters (e.g.: vacancies and defects point). It is possible to influence the thermal conductivity by these parameters with add additives to the UO_2 matrix. The main incentive of the addition of small amounts of oxides to UO_2 fuel such as BeO, Gd_2O_3, and Cr_2O_3 is to improve fuel performance. The beryllium oxide (BeO) has high thermal conductivity and is chemically compatible with UO_2 [1]. The Gd_2O_3 is used as burnable absorbers in UO_2 [2-3]. Nevertheless, the incorporation of Gd_2O_3 in the UO_2 fuel decreases the density and the thermal conductivity. The addition of Cr_2O_3 at low concentrations (e.g., <0.2% by weight) hardly influences the thermophysical properties of UO_2 fuel. The addition of Cr_2O_3 is one of the ways to increase the grain size of UO_2 in order to extend the diffusion path for the fission product gases [4]. The objective of this work is to contribute to data of thermal conductivity of the UO_2 pellets containing additives as BeO; Gd_2O_3 and Cr_2O_3. The content of Cr_2O_3 varied from 0.05 to 0.24wt%; the dopant BeO it ranged 2 and 3 wt% and the gadolinia was kept at 6wt%. These concentrations were considered for having been used in PWR plants as well as in preliminary studies already carried out. The pellets were compacted at pressures of 400 MPa based on the conventional processing of UO_2 pellets obtention with steps of the mixing of powders, pressing, and sintering under a reducing atmosphere. The UO_2 pellets were characterized by density (Archimedes principle) [5] and thermal diffusivity (Flash laser method) [6]. The thermal conductivity was calculated considering each oxide heat capacities.

2. Methodology

The Cr_2O_3 and BeO powders were supplied by Alfa Aesar (99.99% pure), the Gd_2O_3 by Sigma-Aldrich (99.98% pure) and the UO_2 powder was provided by IPEN - Institute of Energy and Nuclear Research. Quantities of each additive were added to uranium dioxide powder and in the following mixed mechanically for 4 h employing a rotating mechanical apparatus. The mixed powders were pressed in pellets form using an especial model of hydraulic press. These green pellets were sintered at 1700 °C for 4 h in an atmosphere of hydrogen using a Mo crucible. The density of each pellet was determined by xylol penetration and immersion method [5] and the pellet mass was taken on Mettler AT201 balance with resolution of 0.1 mg. For thermal diffusivity measurements, the laser flash method was employed in accordance with the ASTM-E-1461-13 standard [6] using abench equipment developed by researchers from the CDTN (Nuclear Technology Development Center). By this method, the front face of a small disk-shaped sample is subjected to a very short burst of radiant energy. The resulting temperature rise of the rear surface of the sample is registered and from the obtained thermogram, the sample thermal diffusivity is calculated. The obtained results were normalized by the following equations [1]:

$$\alpha_{95} = \alpha \cdot \left[\frac{1 - (0.05 \cdot \varepsilon)}{1 - (\varepsilon \cdot P)}\right] \cdot \left[\frac{1 - P}{1 - 0.05}\right] \tag{1}$$

$$\varepsilon = 2.6 - 5x10^{-4} \cdot (T - 273.15) \tag{2}$$

Where α_{95} corresponds to the thermal diffusivity normalized to 95% of theoretical density, α to the determined thermal diffusivity, P to the porosity of the pellets, and T to the temperature. The specific heat capacity values were calculated by the law mixing [1,7] and the thermal conductivity of fuel pellets was determined by product of their thermal diffusivity, density, and specific heat capacity.

The results obtained were compared to fuel pellets of UO_2. The expanded uncertainty was estimated according to the ISO/BIPM Guide to the Expression of Uncertainty in Measurement (GUM) [8].

3. Results and Discussion

Pellet sintered densities are shown in Table I. The maximum expanded relative uncertainty of sintered density pellets was 2%, for a coverage probability of approximately 95%, k=2. The densities obtained by the xylol immersion method were 94%, 95%, from 93% to 94%, and 84% of the theoretical densities (TD) of UO_2, UO_2-BeO, UO_2-Cr_2O_3, and UO_2-Gd_2O_3 fuel pellets, respectively. The addition of gadolinia had a negative effect on density. With the addition of 6% gadolinia the density was reduced by 11% when compared to pure UO_2, possibly due to the formation of porosity. The denser the fuel and the less porous the greater the thermal conductivity. However, the incorporation of chromium and beryllium oxides slightly changed the density value when compared to standard UO_2. Although UO_2 doped with Cr_2O_3 tends to promote densification and grain growth, other factors such as the potential sintering oxygen of the sintering atmosphere may have affected densification and grain growth.

Table I: Sintered pellets density.

Pellets composition	Sintered Density /g·cm^{-3}	%TD
UO_2	10.12	94
	10.27	94
UO_2-2wt%BeO	9.93	95
UO_2-3wt%BeO	9.76	95
UO_2-0.05wt%Cr_2O_3	10.17	93
	10.20	93
UO_2-0.10wt% Cr_2O_3	10.24	94
	10.26	94
UO_2-0.20wt% Cr_2O_3	10.20	93
	10,17	93
UO_2-0.24wt% Cr_2O_3	10.26	94
	10.21	94
UO_2-6wt%Gd_2O_3	8.97	84
	9.00	84

From Table II and Table III are shown the specific heat capacity, normalized thermal diffusivity, and the normalized thermal conductivity both to 95% TD. The maximum expanded relative uncertainty of the thermal diffusivity (coverage factor k = 2) was estimated at 7.5%. The highest deviation between duplicated pellets was of the order of 6%, indicating good reproducibility of the process. The expanded uncertainty for the specific heat capacity was assumed to be 2%, and the maximum expanded uncertainty for thermal conductivity is estimated at 8.0%. Regarding specific heat capacity at room temperature, for the Cr_2O_3 and Gd_2O_3 dopants, the calculated values are almost identical to that of pure UO_2. It is seen that for BeO dopant in UO_2, at high contents there is an increase in heat capacity. The maximum deviation in heat capacity from pure UO_2 to UO_2-3wt%BeO fuel pellets is about 11%. As expected, the thermal diffusivity and thermal conductivity of UO_2 increased with BeO content. The range of the values of thermal diffusivity and conductivity of BeO dopants were 3.28 mm^2·s^{-1} to 3.71 mm^2·s^{-1} and 8.17 W·m^{-1}·K^{-1} to 9.36 W·m^{-1}·K^{-1}, respectively. The thermal conductivity of UO_2-2wt%BeO and UO_2-3wt%BeO fuel pellets were about 17%

and 33% higher than that of UO_2 pellets, respectively. The incorporation of oxides of gadolinium in UO_2 affected the thermal diffusivity and thermal conductivity when compared to the UO_2 pellets. As expected, the presence of gadolinia implies an increase in the population of defects, so the thermal diffusivity and thermal conductivity decrease. The maximum deviation in thermal conductivity of Gd_2O_3 doped UO_2 from that of pure UO_2 is about 27%. It is seen that as the concentration of Cr_2O_3 is increased, the thermal conductivity is increased. Nevertheless, this increase in thermal conductivity is decreased for concentration up to 0.20wt%, probably because of phonon-impurity scattering (substitutional impurity), implying thermal conduction. In Fig. 1, the normalized thermal conductivity is plotted as a function of doped UO_2 for several dopants. A comparison of the thermal conductivity of UO_2 pellets calculated by equations of Ronchi *et al.* [9] and the data obtained here, indicates the quality of the process for obtaining fuel pellets.

Table II: Specific heat capacity of the pellets at 298 K.

Pellets Composition	Specific Heat Capacity $/J\cdot kg^{-1}\cdot K^{-1}$
UO_2	235
UO_2-2wt%BeO	254
UO_2-3wt%BeO	262
UO_2-0.05wt% Cr_2O_3	235
UO_2-0.10wt% Cr_2O_3	236
UO_2-0.20wt% Cr_2O_3	236
UO_2-0.24wt% Cr_2O_3	236
UO_2-6wt%Gd_2O_3	238

Table III: Normalized thermal diffusivity results at 298 K.

Pellets composition	Normalized thermal diffusivity $/mm^2\cdot s^{-1}$	Normalized thermal conductivity $/W\cdot m^{-1}\cdot K^{-1}$
UO_2	2.98	7.19
	2.91	7.03
UO_2-2wt%BeO	3.29	8.19
	3.28	8.17
UO_2-3wt%BeO	3.69	9.31
	3.71	9.36
UO_2-0.05wt%Cr_2O_3	2.93	7.01
	3.06	7.34
UO_2-0.10wt%Cr_2O_3	2.98	7.20
	3.15	7.61
UO_2-0.20wt%Cr_2O_3	3.27	7.88
	3.45	8.29
UO_2-0.24wt%Cr_2O_3	3.04	7.37
	3.21	7.74
UO_2-6wt%Gd_2O_3	2.45	5.23
	2.52	5.41

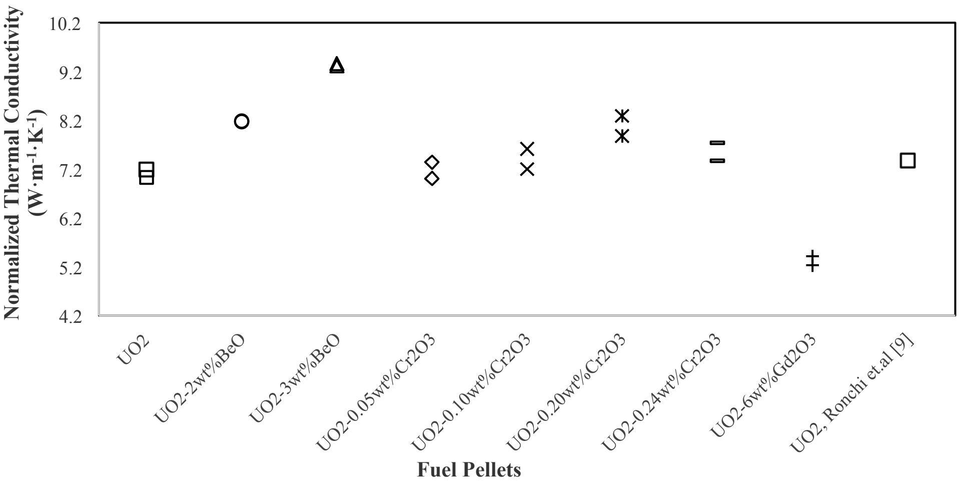

Figure 1: Normalized thermal conductivity of UO_2-base fuel and standard UO_2 fuel.

4. Conclusions

Uranium dioxide pellets for nuclear fuel have been widely used in nuclear power plants, and their low thermal conductivity affects the performance of nuclear fuel. In the present work, we observed that the thermal conductivity of the UO_2-BeO pellets increased with the BeO content and for the UO_2-Gd_2O_3 pellets a substantially lower thermal conductivity was verified, showing that in fact the Gd_2O_3 additive affects the thermal conductivity of the pellets. The fuel doped with Cr_2O_3 had a smaller effect on thermal conductivity when compared to UO_2, which is a good result in case the intention is to increase the grain size of UO_2.

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