Journal of Nuclear Materials 486 (2017) 167–171

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Self-irradiation effect on thermal conductivity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ solid solution

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HIGHLIGHTS

- The authors prepared $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ and measured thermal diffusivity.
- Dependence of thermal conductivity on storage time was clarified.
- After annealing at 1423 K in vacuum, thermal conductivity was recovered.

ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form
25 December 2016
Accepted 16 January 2017
Available online 18 January 2017

Keywords:
$Zr_{0.70}Pu_{0.25}Cm_{0.05}N$
Thermal conductivity
Lattice defects
Self-irradiation
Thermal recovery

ABSTRACT

This study evaluated the dependence of the thermal conductivity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ on storage time and temperature. The authors prepared sintered samples of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ solid solution and measured thermal diffusivity at storage times of 0, 24, 72, 144, 240, 408, 552, 816, 1,680, and 2064 h, from which it was determined that the thermal conductivity decreased exponentially with increasing storage time. This result suggests that the decrease of the thermal conductivity could be attributed to the accumulation of lattice defects from self-irradiation. To confirm the thermal recovery behavior of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ under annealing, thermal diffusivity was also measured just after annealing. The thermal conductivity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ was determined to be larger than that of $Zr_{0.58}Pu_{0.21}Cm_{0.21}N$ but smaller than that of $Zr_{0.80}Pu_{0.10}Cm_{0.10}N$.

1. Introduction

The long-term hazards of radioactive waste arising from nuclear energy production are a topic of serious discussion and a matter of public concern. One option for reducing the long-term radiotoxicity of high-level radioactive waste and increasing the efficiency of repositories is to modify future nuclear fuel cycles by partitioning and transmuting minor actinides (MAs: Np, Am, Cm). So far, accelerator-driven systems (ADS) are being developed as dedicated systems for the transmutation of MA. The ADS designed by JAEA uses (Pu, MA)N fuel diluted by ZrN in a subcritical core [1]. Because of its stability against irradiation and favorable thermal properties, as well as its nuclear inertness, ZrN is seen as a possible diluent for nitride fuel. Consequently, the thermal conductivity of (Zr, Pu, MA)N is important when designing subcritical cores in nitride-fueled ADS.

^{244}Cm has the shortest half-life among Pu and the MAs (18.1 yr) and generally dominates the production of decay heat and the decrease of thermal conductivity during storage [2]. It is important to clarify the dependence of thermal conductivity on the storage time of Cm-containing nitrides, as it is indispensable basic information for the use of Zr-based MA nitride fuels. Recently, the authors clarified the thermal conductivity dependence on storage time of Cm-containing oxides [3,4]. However, experimental barriers associated with a high radioactivity have to date prevented the gathering of experimental data on the dependence of thermal conductivity on the storage time of Cm-containing nitrides.

In this study, the dependence of the thermal conductivity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ on storage time and temperature was measured. Sintered samples of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ solid solution

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http://dx.doi.org/10.1016/j.jnucmat.2017.01.029
0022-3115/

Table 1
Metal element composition in the nitride sample.

Isotope	Half-life (year)	Mole fraction (%)
^{236}U	1.0×10^5	0.1
^{239}Pu	24100	7.0
^{240}Pu	6570	17.9
^{244}Cm	18.1	3.9
^{245}Cm	8500	0.2
^{246}Cm	4730	0.9
Zr	–	70.0

were prepared in order to measure their thermal diffusivity using the laser flash method at elapsed storage times of 0, 24, 72, 144, 240, 408, 552, 816, 1,680, and 2064 h. To confirm this thermal recovery behavior for annealing, the thermal diffusivity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ was also measured just after annealing. The authors used the equation of the self-irradiation lattice expansion model in order to model the dependence of the thermal conductivity on storage time [3].

2. Experimental

2.1. Samples

$Pu_{0.833}Cm_{0.167}N$ samples were prepared via the carbothermic reduction of dioxide mixtures. First, PuO_2 and $Pu_{0.78}Cm_{0.22}O_2$ powders were blended with carbon powder. The mixtures were ground in an agate mortar and compacted into tablets. The tablets were loaded onto a tungsten crucible and heated in flowing N_2 gas at 1673 K for nitridation and then heated in flowing N_2+4%H_2 gas at 1793 K in order to remove residual carbon. The resultant products were ground and mixed with ZrN powder synthesized from Zr metal through its hydride. The mixed powder was pressed into two disks and sintered in a stream of N_2+4%H_2 gas at 1973 K in order to produce $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ solid solution pellets. One sintered pellet was subject to density and thermal diffusivity measurements, while the other was subjected to X-ray analysis and chemical analysis with a view toward characterization. The corresponding isotopic compositions are summarized in Table 1. In the results of Table 1, the effective decay constant in the nitride sample λ was determined using the following equation:

$$\lambda\left(\mathrm{h}^{-1}\right) = \sum_i \frac{\ln 2}{365.24 \times 24 \times t_{1/2i}} w_i, \tag{1}$$

where $t_{1/2i}$, and w_i are the half-life (years) and the mole fraction (%) of each actinide element, respectively. The value of λ was calculated to be 1.73×10^{-7} h^{-1} on the basis of Table 1. The characteristics of the $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ disk samples are summarized in Table 2. The oxygen and nitrogen contents of the samples were measured using a device based on the inert gas fusion technique (HORIBA, EMGA-550). The bulk density evaluated from the dimensions and weight of the sintered sample was 8.40 g/cm^3 (85.9 %TD).

Table 2
Characteristics of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ disk samples.

XRD phases	Cubic (Fcc)
Lattice Parameter (nm)	0.4671
Diameter (mm)	3.085
Thickness (mm)	1.186
Weight (mg)	74.43
Density (g/cm^3)	8.40 (85.9%TD)
Nitrogen (wt%)	9.15
Oxygen (wt%)	0.77

2.2. Thermal diffusivity measurement

The thermal diffusivity was measured using the laser flash method; detailed information on the thermal diffusivity measuring device (ADVANCE-RIKO, TC-7000GB) is given in Refs. [5,6]. Graphite powder was sprayed on both surfaces of the sintered samples in order to prevent transmission of the laser beam. Thermal diffusivity was determined applying a curve fitting method [7,8] to thermal diffusivity measurements performed on both heating and cooling processes under a vacuum with a background pressure of less than 2.0×10^{-4} Pa. The thermal diffusivity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ was measured at cumulative storage times of 0, 24, 72, 144, 240, 408, 552, 816, 1,680, and 2064 h. Following the final storage measurement at 2064 h, the sample was annealed at 1223 K in argon gas atmosphere in a background pressure of less than 2.0×10^{-4} Pa and the thermal diffusivity of the annealed sample was measured again. The initial set of thermal diffusivity measurements to evaluate the dependence of thermal diffusivity on storage time was performed from 473 to 573 K, while the measurements conducted to evaluate the thermal recovery behavior was performed from 473 to 1273 K.

2.3. Determination of thermal conductivity

The measured thermal conductivities K_M were determined using the following equation:

$$K_M\left(\mathrm{Wm^{-1}K^{-1}}\right) = \alpha C_p \rho, \tag{2}$$

where α, C_p, and ρ are the thermal diffusivity, heat capacity, and bulk density, respectively, of the sample. For the purposes of this study, the heat capacity of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ was substituted for that of $Zr_{0.70}Pu_{0.30}N$ [9] and, to enable comparison of the thermal conductivities of the (Zr, Pu, MA)N solid solutions under examination, the data were corrected to 100%TD using the Schulz equation [10]:

$$K_M\left(\mathrm{Wm^{-1}K^{-1}}\right) = K_{\mathrm{TD}}(1-P)^X, \tag{3}$$

where K_{TD} is the thermal conductivity of a sample with 100% TD, P is the porosity of the sample, and the parameter $X = 1.5$ is consistent with spherically shaped closed pores. As reported by Bakker et al. [11], equation (3) was, among a variety of porosity correction formulas, in best agreement with the results of finite element computations over a wide range of porosities up to 0.3.

3. Results and discussion

3.1. Lattice parameter of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$

The samples were subjected to powder X-ray diffraction (XRD) analysis using Cu-Kα radiation to determine lattice parameters and identify phases. The XRD patterns of the $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ samples are shown in Fig. 1 (a). In particular, the (311) peaks are shown in Fig. 1 (b). The XRD measurements were performed at room temperature using samples stored for 77, 597, 933, 1,508, and 2229 h, and it was found that the XRD peak intensity and scattering angle, 2θ, decreased with increasing storage time. Although degradation of crystallinity occurred, the $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ sample retained a single-phase NaCl-type structure over the storage time range investigated. Similarly, the $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ sample remained a nitride solid solution for the length of the assessment (= 2229 h).

The lattice parameter of $Zr_{0.70}Pu_{0.25}Cm_{0.05}N$ was determined using the following self-irradiation lattice parameter model: