



# Thermal expansion and self-irradiation damage in curium nitride lattice



Masahide Takano<sup>a,\*</sup>, Hirokazu Hayashi<sup>a</sup>, Kazuo Minato<sup>b</sup>

<sup>a</sup> Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai-mura, Ibaraki-ken 319-1195, Japan

<sup>b</sup> Nuclear Science Research Institute, Japan Atomic Energy Agency, Tokai-mura, Ibaraki-ken 319-1195, Japan

## ARTICLE INFO

### Article history:

Received 2 July 2013

Accepted 25 January 2014

Available online 3 February 2014

## ABSTRACT

A powder sample of curium nitride (CmN) containing 0.35%–Pu and 3.59%–Am as actinide impurities was prepared by carbothermic nitridation of the oxide. The lattice expansion induced by self-irradiation damage at room temperature was measured as a function of time. The saturated  $\Delta a/a_0$  value was 0.43%, which is greater than those for transuranium dioxides available in literature. The undamaged lattice parameter at  $297 \pm 1$  K was determined to be  $0.50261 \pm 0.00006$  nm. Temperature dependence of the lattice parameter was measured by a high temperature X-ray diffractometer in the temperature range up to 1375 K. The linear thermal expansion from 293 to 1273 K was 0.964% and the corresponding thermal expansion coefficient was  $9.84 \times 10^{-6} \text{ K}^{-1}$ . Comparing with the other actinide nitrides, it was found that CmN lies between the higher expansion nitrides (PuN and AmN) and the lower expansion nitrides (UN and NpN).

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Nitride is considered as one of the candidate fuel materials for the transmutation of minor actinides (MA: Np, Am, Cm), especially for a subcritical core of accelerator driven system (ADS) [1]. In this case, the nitrides of Pu and MAs are diluted with an inert matrix of transition metal nitride such as ZrN or TiN [2,3]. The present authors and coworkers have been studying the synthesis and material properties of transuranium (TRU) nitrides and also their solid solution with ZrN [4–7], which are needed for fuel design works and for understanding the fuel behavior at high temperatures.

As for thermal expansion, one of the important thermophysical properties, we first reported the thermal expansion of NpN, PuN and AmN [8] determined from the temperature dependence of lattice parameter measured by a high-temperature X-ray diffraction (XRD) method. Further we measured the lattice thermal expansion of (Pu,Am)N, (Np,Am)N, (Np,Pu,Am,Cm)N and (Pu,Am,Zr)N [9] to investigate the composition dependence of thermal expansion coefficients for the nitride solid solution samples. However, only the data for CmN as the nitride fuel component has remained unknown because of some difficulties in the sample preparation and in the XRD measurements arising from relatively short half-life of  $^{244}\text{Cm}$  (18.1 y).

\* Corresponding author. Address: Research Gr for High Temperature Science on Fuel Materials, Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, 2-4 Shirakata Shirane, Tokai-mura, Ibaraki-ken 319-1195, Japan. Tel.: +81 29 282 5431; fax: +81 29 282 5495.

E-mail address: [takano.masahide@jaea.go.jp](mailto:takano.masahide@jaea.go.jp) (M. Takano).

In the present study, we successfully extracted Cm from an aged powder of (Pu,Cm)O<sub>2</sub> solid solution, and immediately prepared a powder sample of CmN from the recovered oxide for the high-temperature XRD measurements. The lattice expansion induced by self-irradiation damage at nominal room temperature was measured to determine the undamaged lattice parameter in advance. The linear thermal expansion of the lattice was then determined in the temperature range from 293 to 1375 K, and was compared with those of other actinide nitrides.

## 2. Experimental

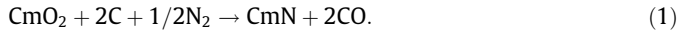
### 2.1. Sample preparation

About 50 mg of (Pu<sub>0.74</sub>Cm<sub>0.26</sub>)O<sub>2</sub> solid solution powder, in which  $^{240}\text{Pu}$  had been accumulated by  $\alpha$ -decay of  $^{244}\text{Cm}$  over a long term storage, was dissolved into a mixed solution of 9 M nitric acid and hydrogen peroxide at 373 K. The hydrogen peroxide solution was added again to reduce Pu(IV) and Pu(VI) ions to Pu(III), followed by exposure to the air atmosphere for 4 days to control the Pu ion to Pu(IV). The prepared solution containing Pu(IV) and Cm(III) ions was then passed through a column filled with the anion-exchange resin (Bio-Rad AG1 1-x4, 200–400 mesh) followed by 6.6 M nitric acid to remove Pu(IV) ions. This separation process was repeated and thus the Cm-fraction solution was obtained. The details of the separation process have been described elsewhere [10].

The precipitation of Cm oxalate was prepared by adding oxalic acid to the solution under the condition of 0.25 M nitric acid–0.1 M oxalic acid. The supernatant fraction was removed and the

precipitation was washed 3 times with 5 ml of water. After dehydration using a hotplate, about 12 mg of Cm oxalate was obtained. The white fine powder collected into a platinum crucible was heat-treated at 1143 K for 3 h in an O<sub>2</sub> gas stream, and thus the black powder of CmO<sub>2</sub> was obtained by cooling slowly under 673 K.

The CmN sample was synthesized by carbothermic nitridation of the oxide. The total reaction can be formally expressed by



About 7 mg of the oxide powder was blended with amorphous carbon powder at C/Cm atomic ratio of 4.0, which corresponds to 200% of the theoretically required carbon, in order to suppress the dissolved oxygen in the nitride product as low as possible. The mixture was pressed into a thin tablet with diameter of 3.15 mm, and then it was put into a tungsten crucible for nitridation.

Since the exact temperature for the nitridation of Cm oxide was unknown, the heating conditions for syntheses of (Pu,Cm)N [11] and (Np,Pu,Am,Cm)N [9] were applied instead. The mixture was heat-treated in a purified N<sub>2</sub> gas stream of 2 l/min and the temperature was raised gradually from 1573 K to 1703 K in 2 h for nitridation. Subsequently the nitride was heat-treated at 1793 K in a purified N<sub>2</sub> + 4%H<sub>2</sub> mixed gas stream for 5.5 h to remove the residual carbon. The volatilization loss of Cm during the heat treatment was estimated to be 3% from the mass balance, assuming that the excess carbon was removed completely.

A part of the nitride sample was dissolved into nitric acid after all the XRD measurements to determine the isotopic composition by  $\alpha$  and  $\gamma$  spectrometry. The result of analysis is shown in Table 1. The contents of <sup>246,247,248</sup>Cm were calculated from that of <sup>244</sup>Cm, based on the known Cm isotopic composition. As the actinide impurities, 0.35 at.-%-Pu and 3.59 at.-%-Am were included as the solid solution (Cm,Am,Pu)N. The total Cm purity was then determined to be 96 at.%. Most part of <sup>243</sup>Am was included in the original (Pu,Cm)O<sub>2</sub> powder and was remained with Cm after the purification. <sup>241</sup>Am and some part of <sup>243</sup>Am might be contamination from the furnace for nitridation, which had been used many times for the synthesis of volatile <sup>241</sup>AmN and <sup>243</sup>AmN. The effective decay constant,  $\lambda$ , in the nitride sample was calculated to be  $9.43 \times 10^{-10} \text{ s}^{-1}$  according to the following definition,

$$\lambda = \sum_i \lambda_i x_i \quad (2)$$

where  $\lambda_i$  is the decay constant and  $x_i$  the atomic fraction of isotope  $i$  contained in the sample.

## 2.2. X-ray diffraction measurements

The porous CmN tablet obtained by the carbothermic synthesis was heat-treated again at 1473 K for 1.5 h in the N<sub>2</sub> + 4%H<sub>2</sub> mixed gas stream for annealing just before the XRD measurements. About 5 mg of the powdered sample was mounted on a tungsten holder,

and then it was loaded on the sample stage/heater of the diffractometer. The apparatus and measurement technique were described in the previous paper [8]. The whole process of Cm oxide and nitride preparation, and the XRD measurements with Mo K $\alpha$  radiation were carried out in hot cells and a glove box under a purified argon atmosphere.

Prior to the high-temperature measurements, the lattice parameter change induced by the self-irradiation damage at room temperature ( $297 \pm 1 \text{ K}$ ) was measured as a function of time until it reached a constant value, in order to determine the undamaged value of lattice parameter. The measurements were repeated 20 times in 3 days without the lid of sample chamber, i.e. the powder sample was being exposed to the argon atmosphere of the glove box, in which the moisture content was around 2–3 ppm. Although the lattice parameter was saturated to a constant value within this duration, the peak intensity decreased to half of the initial state.

To confirm the possible cause of the decrease in peak intensity, whether it was the influence of self-irradiation damage or the hydrolytic reaction with moisture in the atmosphere, the sample was heated to 1073 K in the closed sample chamber with the purified N<sub>2</sub> gas stream. Diffraction peaks of the nitride almost disappeared during the heating process and the light gray powder was obtained. That means the CmN powder gradually reacted with moisture in the argon gas to form amorphous hydroxide at room temperature in 3 days [5], and the hydroxide decomposed to the sesquioxide during the heating process. The high dose rate of <sup>244</sup>Cm may have activated the reaction of nitride with moisture. Therefore, the powder was mixed with the carbon and nitrated again with the same method described in Section 2.1 for the high-temperature XRD measurements.

The fresh CmN powder was again loaded on the sample stage of the diffractometer just after nitridation, and the purified N<sub>2</sub> gas stream was applied into the leak-tight sample chamber. To eliminate the influence of self-irradiation damage, the sample was immediately heated to 1280 K and held for 1 h. Then the high-temperature XRD measurements were performed sequentially at 1280, 1173, 1073, 971, 873, 776, and 298 K. On the next day, the sample was heated again to 1375 K and the measurements were performed at 1375 and 675 K.

The sample temperature was monitored by a R-type thermocouple (Pt/Pt-13Rh) inserted into the thin sample holder (2 mm in thickness). The temperature fluctuation during each XRD measurement was within  $\pm 1 \text{ K}$ . At each temperature, the lattice parameters calculated from seven K $\alpha$ 1 peak positions between (3 3 1) and (7 3 1) reflections were extrapolated to  $2\theta = 180^\circ$  using Nelson–Riley function for refinement. The maximum error in determination was  $\pm 0.00007 \text{ nm}$  at the highest temperature 1375 K.

## 3. Results and discussion

### 3.1. Expansion induced by self-irradiation damage

The partial XRD profile of the CmN powder recorded at room temperature is shown in Fig. 1. The sample was identified as a single-phase nitride solid solution with the NaCl-type structure as expected. The K $\alpha$ 1–K $\alpha$ 2 resolution was fine enough to determine the K $\alpha$ 1 peak positions precisely. Although the light element impurities (oxygen and carbon) were not analyzed, the oxide phases were below detectable level.

Fig. 2 shows the change in lattice parameter at room temperature as a function of storage time after heat treatment. The lattice parameter of CmN increased with time due to the accumulation of Frenkel defect from 0.50278 nm at 1.8 h to 0.50475 nm at 76 h, at which it reached almost a constant value. The specific heat generation in the sample was calculated to be 527 W/mol from  $\alpha$ -decay

**Table 1**  
Isotopic composition in the CmN sample determined by  $\alpha$  and  $\gamma$  spectrometry.

Isotope	Content (at.%)
<sup>240</sup> Pu	0.35
<sup>241</sup> Am	0.23
<sup>243</sup> Am	3.36
<sup>244</sup> Cm	77.61
<sup>245</sup> Cm	2.87
<sup>246</sup> Cm	15.18
<sup>247</sup> Cm	0.25
<sup>248</sup> Cm	0.15
Pu/Am/Cm = 0.35/3.59/96.06 (at.%)	

Download English Version:

<https://daneshyari.com/en/article/7967929>

Download Persian Version:

<https://daneshyari.com/article/7967929>

[Daneshyari.com](https://daneshyari.com)