Carbothermic synthesis of (Cm, Pu)N

Masahide Takano [a,*,1], Akinori Itoh [a], Mitsuo Akabori [a], Toru Ogawa [a], Masami Numata [b], Hisato Okamoto [b]

[a] *Department of Materials science, Research Group for Actinides Science, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan*
[b] *Department of Hot Laboratory, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan*

Abstract

Nitrides are being considered as fuel candidates for the transmutation of minor actinides. Carbothermic reduction of oxides is an effective method to fabricate nitride fuels. In this study, $(Cm_{0.40}, Pu_{0.60})N$ was synthesized by the carbothermic reduction of the mixed oxide in N_2. By applying excess carbon, an oxide-free nitride was obtained at 1773 K. The lattice parameter of the oxide-free sample was 0.4948 nm, and that of the nitride with oxides was 0.4974 nm. The former value agreed well with that estimated from the literature values for CmN and PuN. The larger lattice parameter of the latter sample is considered to be due to the oxygen dissolved in the nitride. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Nitride fuels have several advantages such as high melting points and high densities of metallic elements. Another anticipated advantage is the mutual miscibility among actinides nitrides. Arai et al. [1,2] have prepared the solid solutions of mononitrides among lighter actinides (UN, NpN and PuN). As part of this study, we have confirmed the formation of a solid solution (Am,Y)N [3]. This work suggests that nitrides of some transition metals such as ZrN or YN may be suitable as the neutronically inert matrix for targets in the accelerator driven systems (ADSs).

Carbothermic reduction of oxides is a viable method for fabricating UN and PuN fuels for fast breeder reactors [1,4,5]. The direct reaction of metal and nitrogen gas is suitable to obtain small quantities of high-purity material. From the fuel fabrication viewpoint, carbothermic reduction is attractive for large-scale production, since oxides are readily available from the existing fuel reprocessing cycle. In this study, we applied carbothermic reduction to synthesize the Cm and Pu mixed nitride. The purpose is to confirm the mutual miscibility among the nitrides of lighter and heavier actinides.

2. Experimental

2.1. Material

$(Cm, Pu)O_2$ powder was used as the starting material. It was originally $^{244}CmO_2$; however, considerable amounts of ^{240}Pu have formed by the decay of ^{244}Cm during 30 years of storage. The composition of actinides elements was determined by alpha spectrometry. The sample was prepared by dissolving 12 mg of the powder in 100 ml of 8 N nitric acid with a drop of hydrogen fluoride. Complete dissolution was achieved by heating to ∼350 K. The solution was then diluted with the nitric acid to 1000/1, to reduce the broad shoulder of the strong peak of ^{244}Cm in the spectrum so that other peaks could be detected clearly. Each sample was then baked to dry on a stainless-steel dish. For each sample, the spectrum was obtained and analyzed quantitatively

---

* Corresponding author. Present address: Oak Ridge National Laboratory, P.O. Box 2008, MS 6375, Oak Ridge, TN 37831-6375, USA. Tel.: +1-865 574 0846; fax: +1-865 574 4987.

E-mail address: takano@popsvr.tokai.jaeri.go.jp (M. Takano).

[1] I will stay in Oak Ridge National Laboratory from August 14, 2000 to August 2, 2001, based on the exchange visitor program between JAERI and ORNL.

using the dominant peaks of [238]Pu, [240]Pu, [244]Cm and [246]Cm. The results of the analysis are listed in Table 1 together with the half-lives [6]. X-ray diffraction analysis was performed to determine the chemical form of the sample using a wide-angle goniometer with CuKα radiation. Due to the self-irradiation damage of [244]CmO_2, the sample was annealed at 643 K in air for 7 days [7]. The lattice parameter was determined before and after the annealing period. Judging from the half-lives in Table 1, the alpha decay of [244]Cm was considered to be the dominant factor in the lattice parameter expansion. From these analyses, the powder was determined to be a single phase of $(Cm_{0.40}, Pu_{0.60})O_{2-x}$ with a fluorite structure.

2.2. Carbothermic synthesis

Two samples were synthesized. A schematic diagram of the system used is shown in Fig. 1. In the first run (Sample 1), about 30 mg of the oxide was mixed with graphite powder at a C/M (M = Cm + Pu) initial molar ratio of 3.2. The mixture was heated in a molybdenum

Table 1
Results of alpha-spectrometry on the starting material of $(Cm, Pu)O_2$, together with half-lives ($T_{1/2}$)

Isotopes	$T_{1/2}$ (year)	Fraction (mol%)
[238]Pu	87.7	0.1
[240]Pu	6570	60.2
[244]Cm	18.1	35.8
[246]Cm	4700	3.9

crucible to 1773 K in a nitrogen gas stream with a flow rate of 1 l/min. The CO gas release was measured continuously by an infrared spectrometer to monitor the conversion of the oxide to the nitride. The formation of the nitride is formally expressed by

$$(Cm, Pu)O_{2-x} + (2-x)C + 1/2N_2$$
$$\rightarrow (Cm, Pu)N + (2-x)CO.$$
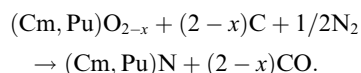
After the CO gas release subsided, the gas was changed to a 4% hydrogen in nitrogen mixed gas stream to remove residual carbon, and the sample was heated until the CO gas release subsided again. In the second run (Sample 2), the C/M ratio was chosen as 1.6 (which is smaller than the stoichiometric C/M ratio) to study the effect of excess oxygen. The mixture was heated at 1743 K in the nitrogen gas stream until the CO gas release subsided.

2.3. X-ray diffraction

After the synthesis, the products were kept in the furnace overnight due to the limited working-time of the facility. According to Noe and Fuger [7], lattice parameter expansion of [244]CmO_2 by self-irradiation damage is very quick and saturates almost within ~4 days. To anneal the lattice damage, the products were heated again at 1473 K in the hydrogen and nitrogen mixed gas stream for 3 h on the day after the synthesis. The product was then ground and mounted on a sample holder with epoxy resin. The surface was sealed with 50 μm polyimide film to minimize the hydrolysis of the
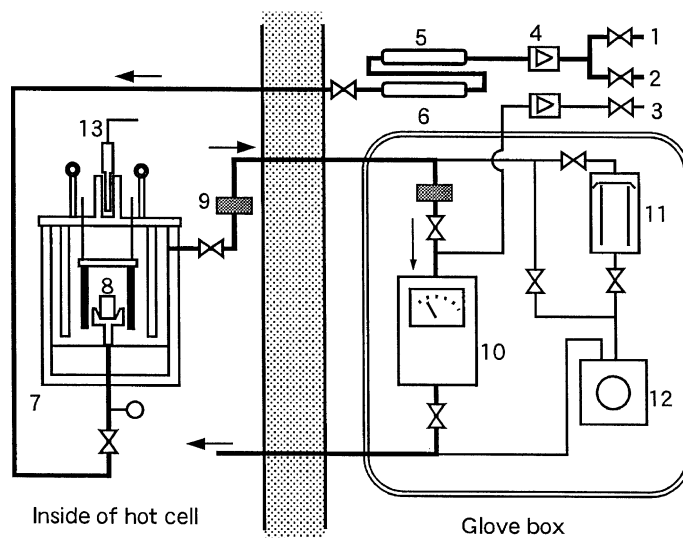

Fig. 1. Schematic diagram of the system for carbothermic reduction: 1. N_2 gas, 2. $N_2 + 4\%H_2$ gas, 3. Ar + CO std. gas, 4. mass-flow controller, 5. dry column, 6. oxygen getter, 7. furnace with C/C composite heater, 8. Mo crucible, 9. filter, 10. CO monitor, 11. diffusion pump, 12. rotary pump, 13. radiation thermometer.

nitride. XRD profiles were obtained by 0.02° step scanning between 20° and 120°. The diffraction angle was calibrated with an internal Si standard mounted on the same sample holder.

3. Results and discussion

The CO gas release behavior during carbothermic reduction showed that the heating temperature of 1773 K for Sample 1 was enough to get a complete reaction. Although vaporization loss of Pu and/or Cm during the process may change their molar ratio, the equilibrium vapor pressure of pure Cm and Pu metals are close to each other and the vaporization loss of Pu at the temperature is negligible in literatures [8,9].

The characteristic parts of the XRD profiles of Samples 1 and 2 are shown in Fig. 2. The results are summarized in Table 2. In both samples, formation of the solid solution $(Cm, Pu)N$ was confirmed. Oxides coexisted with the nitride in Sample 2 because of an insufficient amount of carbon to reduce the whole oxide. The remaining oxides were not solid solutions but indexed as the mixture of monoclinic Cm_2O_3 and a Pu oxide with a bcc-structure (see Fig. 2).

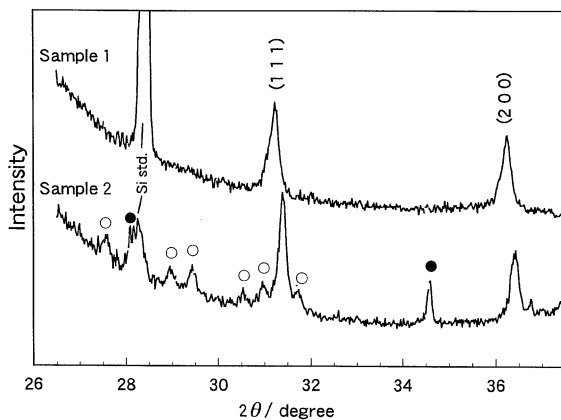The initial C/M ratio of 3.2 for Sample 1 was necessary to ensure contact between the oxide and carbon particles closer. The free carbon remaining in the products would be removed by heating in hydrogen and nitrogen mixed gas, because carbides of heavier actinides (Am and probably Cm) are more unstable than those of lighter actinides [10].

The lattice parameters of the nitride were 0.4948 nm for Sample 1 and 0.4974 nm for Sample 2, respectively, which were obtained at 6–7 h after the annealing. Although the quantitative analysis of oxygen and carbon impurities have not been done, the larger lattice parameter of Sample 2 is considered to be due to oxygen in the nitride. The increase in lattice parameters with oxygen content has been confirmed in the case of PuN by Jain and Ganguly [11]. A similar effect of oxygen impurity has also been observed for AmN [12,13].

Fig. 3 shows the lattice parameter expansion vs. time after annealing for Sample 1. Although only a limited number of data points were obtained and the lattice parameter may have been affected by the hydrolysis, the 'damage-free' value was estimated to be 0.4943 ± 0.0002
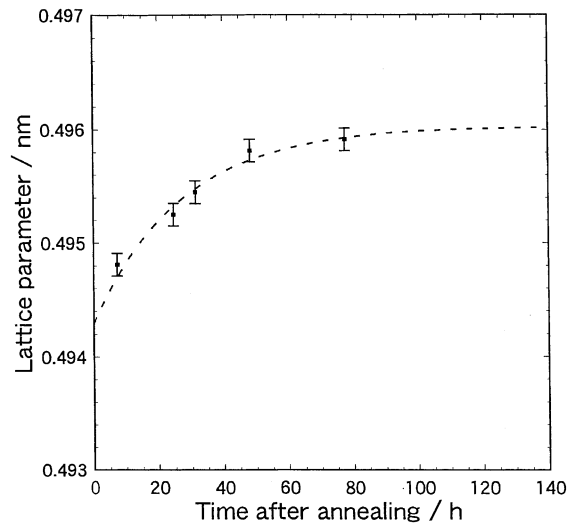
Fig. 2. XRD profiles of Samples 1 and 2. Open circles show monoclinic Cm_2O_3 and closed circles a Pu oxide with a bcc-structure.

Fig. 3. Lattice parameter expansion of $(Cm, Pu)N$ by self-irradiation damage.

Table 2
Conditions of syntheses and results of XRD analyses on Samples 1 and 2

Sample no.	C/M molar ratio	Temperature (K)	Gas (Time)	Phase in product	Lattice parameter (nm)
1	3.2	1773	N_2 (4h) $N_2 + 4\%H_2$ (4h)	$(Cm_{0.40}, Pu_{0.60})N$	0.4948 ± 0.0001
2	1.6	1743	N_2 (5h)	$(Cm_{0.40}, Pu_{0.60})N$ B–Cm_2O_3 + bcc Pu–O	0.4974 ± 0.0002
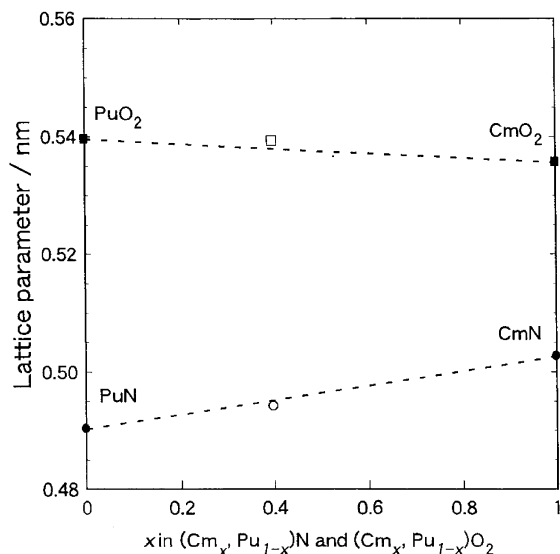
Fig. 4. Comparison of the lattice parameters of $(Cm_{0.40}, Pu_{0.60})N$ and $(Cm_{0.40}, Pu_{0.60})O_{2-x}$ with the literature values for CmN, PuN (closed circles), CmO_2 and PuO_2 (closed squares), respectively. Open circle shows the estimated 'damage-free' value for Sample 1, open square the value for the starting material at 6 h after annealing.

nm. This value was obtained by fitting the expansion with the equation

$$a(t) = a_0 + A[1 - \exp(-Bt)],$$

where $a(t)$ is the lattice parameter at time t after annealing, a_0 the damage-free lattice parameter at $t = 0$, A and B the constants. Fig. 4 compares the damage-free value for Sample 1 with the literature values of 0.49033 nm for PuN [14] and 0.5027 nm for ^{248}CmN [15] prepared from the metals, as well as similar comparison for the dioxides [7,16]. The lattice parameter of $(Cm_{0.40}, Pu_{0.60})N$ expected from the Vegard's law is 0.4953 nm, which is close to that of Sample 1. Judging from the considerations above, the oxygen content in Sample 1 was not so different from that of nitrides prepared from metals.

4. Conclusions

Single phase $(Cm_{0.40}, Pu_{0.60})N$ was successfully synthesized by the carbothermic reduction of $(Cm_{0.40}, Pu_{0.60})O_{2-x}$ at 1773 K in N_2. The lattice parameter of the oxides-free nitride was 0.4948 nm, close to that expected from the literature values for CmN and PuN. The

mutual miscibility between CmN and PuN was confirmed. This is a significant advantage of nitride fuels for the transmutation of minor actinides, and will make fuel design and fabrication more flexible.

References

[1] Y. Arai, S. Fukushima, K. Shiozawa, M. Handa, J. Nucl. Mater. 168 (1989) 280.
[2] Y. Arai, K. Nakajima, Y. Suzuki, J. Alloys Comp. 271–273 (1998) 602.
[3] M. Akabori, M. Takano, A. Itoh, T. Ogawa, M. Numata, M. Shindo, in: Proc. 30iemes Journees des Actinides, Dresden, Germany, May 4–6, 2000, p. 43.
[4] R.B. Matthews, K.M. Chidester, C.W. Hoth, R.E. Mason, R.L. Petty, J. Nucl. Mater. 151 (1988) 334.
[5] C. Ganguly, P.V. Hedge, A.K. Sengupta, J. Nucl. Mater. 178 (1991) 234.
[6] M. Lederer, V. Shirley (Eds.), Table of Isotopes, 7th Ed., Wiley/Interscience, New York, 1978.
[7] M. Noe, J. Fuger, Inorg. Nucl. Chem. Lett. 7 (1971) 421.
[8] Y. Suzuki, Y. Arai, T. Sasayama, J. Nucl. Mater. 115 (1983) 331.
[9] Y. Suzuki, A. Maeda, Y. Arai, T. Ohmichi, J. Nucl. Mater. 188 (1992) 239.
[10] C.E. Holley Jr., M.H. Rand, E.K. Storms, The Chemical Thermodynamics of Actinide Elements and Compounds, Pt. 6, The Actinides Carbides, IAEA, Vienna, 1984.
[11] G.C. Jain, C. Ganguly, J. Nucl. Mater. 202 (1993) 245.
[12] M. Takano, A. Itoh, M. Akabori, T. Ogawa, S. Kikkawa, H. Okamoto, in: Proceedings of the International Conference on Future Nuclear Systems (Global'99), Jackson Hole, USA, August 29–September 3, 1999.
[13] V.M. Radchenko, M.A. Ryabinin, A.G. Seleznev, E.V. Shimbarev, L.V. Sudakov, I.I. Kapshukov, V.Ya. Vasil'ev, Radiokhimiya 24 (2) (1982) 173.
[14] N.J. Bridger, R.M. Dell, Research on Plutonium Nitride, AERE-R-5441, 1967.
[15] D.A. Damien, R.G. Haire, C.R. Peterson, CONF 780823-8, 1978.
[16] E.H.P. Cordfunke, R.J.M. Konings (Eds.), Thermochemical Data for Reactor Materials and Fission Products, North-Holland, Amsterdam, 1990, p. 292.