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Fabrication of nitride fuels for transmutation of minor actinides

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Abstract

At the Japan Atomic Energy Research Institute, the concept of the transmutation of minor actinides (MA: Np, Am and Cm) with accelerator-driven systems is being studied. The MA nitride fuel has been chosen as a candidate because of the possible mutual solubility among the actinide mononitrides and excellent thermal properties besides supporting hard neutron spectrum. MA nitrides of NpN, (Np, Pu)N, (Np, U)N, AmN, (Am, Y)N, (Am, Zr)N and (Cm, Pu)N were prepared from the oxides by the carbothermic reduction method. The prepared MA nitrides were examined by X-ray diffraction and the contents of impurities of oxygen and carbon were measured. The fabrication conditions for MA nitrides were improved so as to reduce the impurity contents. For an irradiation test of U-free nitride fuels, pellets of (Pu, Zr)N and PuN + TiN were prepared and a He-bonded fuel pin was fabricated. The irradiation test started in May 2002 and will go on for two years in the Japan Materials Testing Reactor.

1. Introduction

The partitioning-transmutation (P-T) study in Japan has been made within the so-called OMEGA project since 1988. The Japan Atomic Energy Research Institute (JAERI) has proposed the concept of the double-strata fuel cycle [1]. The first stratum is the power-reactor fuel cycle and the second stratum the actinide burner cycle, as shown in Fig. 1. The minor actinides (MA: Np, Am and Cm) partitioned from the high-level liquid wastes (HLLW) of the first stratum are fed into the second stratum, where they are transmuted to fission products. In this concept, the power-reactor fuel cycle and the actinide burner cycle may be optimized independently for the safe and economical use of plutonium and the efficient reduction of long-lived hazards, respectively.

For the actinide burner cycle, accelerator-driven systems (ADS) are being studied at JAERI to transmute MA, where MA nitride is adopted as a fuel material of the subcritical core [2]. The nitride fuel has been chosen as a candidate because of the possible mutual solubility of the actinide mononitrides and the excellent thermal properties. In addition, it supports a hard neutron spectrum needed for fissions of the minor actinides. As the second stratum is the dedicated fuel cycle for the burning of the MA, the main components of the fuel should be the MA without uranium that would be converted into the MA through neutron captures and decays. An inert matrix needs to be added to the fuel for the ADS core to suppress a large reactivity change and adjust an adequate linear heat rate during the operation. Highly enriched N-15 would have to be used for the nitride fuel in order to prevent the formation of hazardous C-14 through the reaction $^{14}N(n, p)^{14}C$. By applying a pyrochemical process in the treatment of the spent fuel, N-15 could be readily recovered and recycled [3]. The pyrochemical reprocessing of the nitride fuel has been studied at JAERI [4–9].

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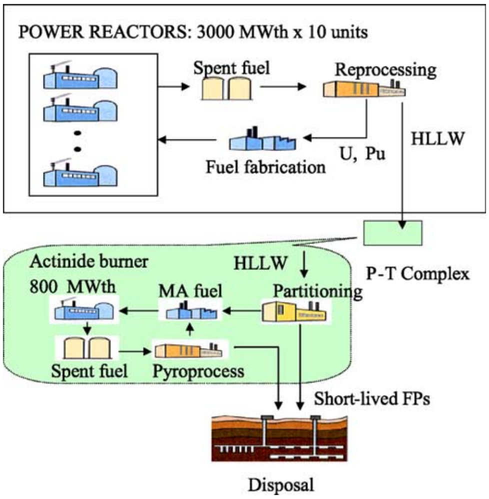

Fig. 1. Double-strata fuel cycle concept.

The present paper gives an overview of the research on the fabrication of the nitride fuels for transmutation of MA performed at JAERI.

2. Fabrication of MA nitrides

2.1. NpN and (Np, Pu)N

NpN was fabricated by carbothermic reduction of NpO_2 in the glove boxes with purified Ar gas atmosphere at the Plutonium Fuel Research Facility (PFRF) of JAERI [10]. Powders of NpO_2 and graphite were mixed at a molar ratio C/NpO_2 of 2.2, which is slightly larger than the stoichiometric value. The excess of graphite powder was added to the oxide to avoid residues of the oxide phase in the product. The mixed powder was heated at 1823 K in flowing N_2 gas for carbothermic reduction and successively heated at 1723 K in flowing N_2–H_2 mixed gas to remove the residual carbon. The X-ray diffraction analysis revealed that NpN was obtained without residual oxide phase. The carbon and oxygen contents, determined by combustion coulometry and inert gas fusion coulometry, were less than 1000 ppm, respectively.

UN and PuN were also fabricated by the same method [11]. The oxygen contents could be limited to less than 1000 ppm with relative ease. The carbon contents remaining in UN, NpN and PuN decreased in this order; for example, 1800, 900 and 300 ppm. This might be caused by the solubility of carbon in respective mononitrides [10].

(Np, Pu)N was fabricated by mixing the powders of NpN and PuN and heating the mixed powder in flowing N_2–H_2 at 2023 K [12]. The X-ray diffraction analysis revealed a single phase of NaCl-type structure and the formation of the complete solid solution. The lattice parameters of (Np, Pu)N as a function of Pu content measured are shown in Fig. 2 [13].

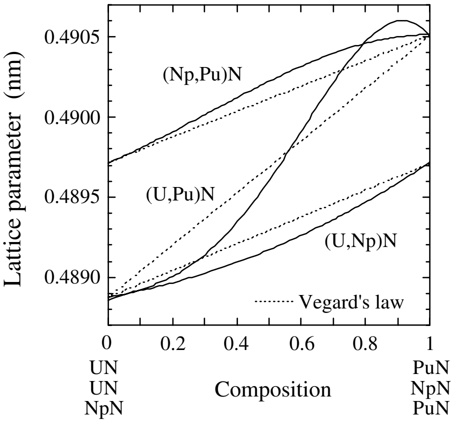

Fig. 2. Lattice parameters of solid solutions of (Np, Pu)N, together with those of (U, Np)N and (U, Pu)N.

Disks of NpN and (Np, Pu)N with more than 90% of the theoretical density were prepared and the thermal diffusivities of NpN and (Np, Pu)N [14,15], the specific heat capacities of NpN [16], and the vaporization behaviors of NpN and (Np, Pu)N [17,18] have been obtained.

2.2. AmN

The fabrication experiments of AmN were made at the Waste Safety Testing Facility (WASTEF) of JAERI. AmN was synthesized from AmO_2 by the carbothermic reduction method [19,20]. The powder of $^{243}AmO_2$, purchased from the State Scientific Center of Russia, was mixed with the excess amount of carbon black powder. About 20 mg of AmO_2 was used in a batch. The mixed powder was heated in a molybdenum crucible at 1573 K for 2 h in flowing N_2 gas and then heated at 1773 K for 2 h in flowing N_2–4%H_2 gas. As the vapor pressure of Am is high compared with those of U and Pu, the heating temperature was lowered from 1823 to 1573 K. During the heating, CO gas release was monitored with infrared spectroscopy to observe the progress of the reaction.

The products obtained were ground and mixed with Si powder as an internal standard for X-ray diffraction analysis. The measurements were started within a day after the synthesis to minimize the effect of self-radiation damage accumulated in the lattice. The X-ray diffraction analysis revealed that AmN without oxide phases was obtained. Fig. 3 shows the X-ray diffraction pattern of AmN and the lattice parameter was determined to be 0.4991 nm [20]. The carbon and oxygen contents were less than 200 and 500 ppm, respectively.

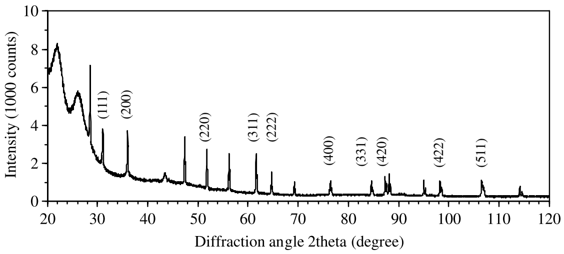

Fig. 3. X-ray diffraction pattern of AmN.

2.3. (Cm, Pu)N

The fabrication experiments of (Cm, Pu)N were made in the hot cell at WASTEF. $(Cm_{0.4}Pu_{0.6})N$ was fabricated from the mixed powder of $(Cm_{0.4}Pu_{0.6})O_2$ and carbon black by the carbothermic reduction method [21]. $(Cm_{0.4}Pu_{0.6})O_2$ was originally $^{244}CmO_2$, which was purchased from the Oak Ridge National Laboratory about 30 years ago. ^{240}Pu is the daughter of ^{244}Cm ($T_{1/2} = 18.1$ year). About 30 mg of the oxide was used in a batch. The mixture was heated at 1773 K in flowing N_2 and N_2–4%H_2 successively.

Before the X-ray diffraction analysis, the samples were heated again at 1473 K in flowing N_2–4%H_2 to anneal the self-radiation damage accumulated in the lattice. The X-ray diffraction patterns were measured repeatedly to clarify the time dependence. The X-ray diffraction analysis revealed the formation of solid solution of $(Cm_{0.4}Pu_{0.6})N$ without residual oxides. As shown in Fig. 4 [21], the lattice parameter of $(Cm_{0.4}Pu_{0.6})N$, which was the estimated damage-free value, almost agreed with the value estimated from Vegard's law between CmN and PuN. This result confirmed the mutual miscibility of CmN and PuN.

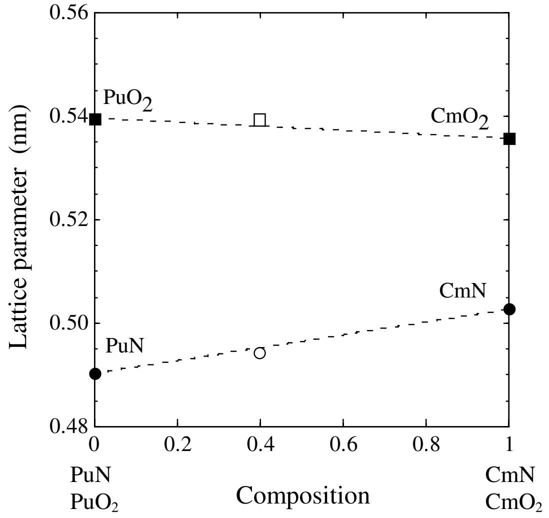

Fig. 4. Lattice parameters of $(Cm_{0.4}Pu_{0.6})N$ and $(Cm_{0.4}Pu_{0.6})O_2$ solid solutions.

3. Fabrication of actinide nitrides with inert matrix

3.1. (Am, Y)N

Solid solutions of (Am, Y)N were prepared by the carbothermic reduction of the mixed powder of $^{243}AmO_2$, Y_2O_3 and excess amount of carbon black [22,23]. The mass of the mixed powder was about 40–50 mg in a batch. The conversion of AmO_2 into AmN should be performed below 1573 K in flowing N_2 to avoid Am vaporization, but this temperature was found to be too low to convert Y_2O_3 into YN. The heating of the mixture was therefore carried out at 1573 K in flowing N_2 to obtain AmN and then at 1773 K to obtain (Am, Y)N, followed by the heating at 1773 K in flowing N_2–4%H_2 to remove the residual carbon. The release of CO gas was monitored during the heating to see the progress of the reactions.

The products obtained were examined by X-ray diffraction analysis. The samples were well grounded in an agate mortar in a glove box with Ar gas atmosphere. The measurements were performed within a few days to minimize the effect of self-radiation damage. It was found from the X-ray diffraction analysis that the solid solution of (Am, Y)N with NaCl-type structure was obtained without any oxide phases. The lattice parameters were close to the values assumed by Vegard's law between AmN and YN, as shown in Fig. 5 [23].

3.2. (Am, Zr)N

Solid solutions of (Am, Zr)N were prepared by the carbothermic reduction method [23]. The powders of $^{243}AmO_2$, ZrO_2 and carbon black were mixed and heated. The total weight of the mixed powder was about 40–50 mg in a batch. As the conversion of ZrO_2 into ZrN could be made easily at 1573 K in flowing N_2 gas,

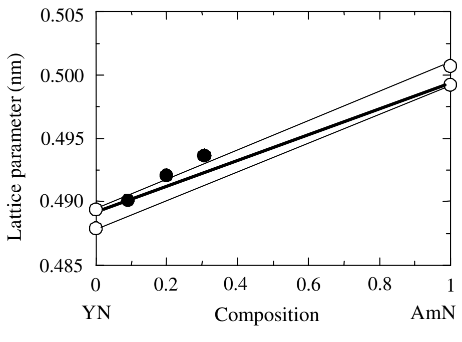

Fig. 5. Lattice parameters of solid solutions of (Am, Y)N.

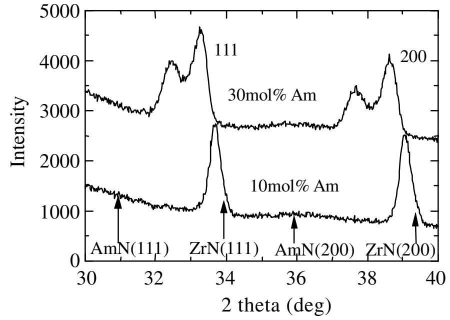

Fig. 6. X-ray diffraction patterns of (Am, Zr)N.

the mixture was heated at 1573 K in flowing N_2 gas to obtain (Am, Zr)N and successively heated at 1773 K in flowing N_2–4%H_2 to remove the residual carbon.

The X-ray diffraction analysis was made with the same procedure as that for (Am,Y)N. Fig. 6 shows the X-ray diffraction patterns of the products with Am contents Am/(Am + Zr) of 10 and 30 mol% [23]. In case of an Am content of 10 mol%, a single phase of solid solution $(Am_{0.1}Zr_{0.9})N$ of NaCl-type structure was obtained without oxide phases. The lattice parameter of $(Am_{0.1}Zr_{0.9})N$ obtained was 0.4636 nm, which was in good agreement with the estimated value using Vegard's law between AmN and ZrN. For the sample with Am content of 30 mol%, each diffraction peak of NaCl-type structure was split into two peaks, while no diffraction peak of the oxides was observed. The result means that the product was mixture of two solid solutions of (Am,Zr)N with different Am contents. From the lattice parameters of the two solid solutions, the Am contents were estimated to be 14.5 and 43.1 mol%. Additional experiments need to be made to clarify the formation of the two solid solution phases.

3.3. (Pu, Zr)N

PuN pellets containing ZrN were fabricated by the classical mechanical blending method [24,25]. PuN was prepared by the carbothermic reduction of PuO_2. The mixed powder of PuO_2 and graphite was compacted into thin disks and heated at 1823 K in flowing N_2 and at 1723 K in flowing N_2–H_2. The pellets of (Pu, Zr)N were prepared by mechanical blending of powders of PuN and ZrN, which was obtained from CERAC Inc. The mixed powder was compacted into thin disks and then heated in flowing N_2–H_2 at 1673 K for 5 h for homogenization. After repeating the procedure of mixing, compacting and heating for three times, the disks were ground and compacted into green pellets under a pressure of about 300 MPa without any organic binder. The green pellets were sintered at 2003 K in flowing Ar, followed by heating at 1673 K in flowing N_2–H_2 for the control of stoichiometry. The density of the pellets was above 90%TD.

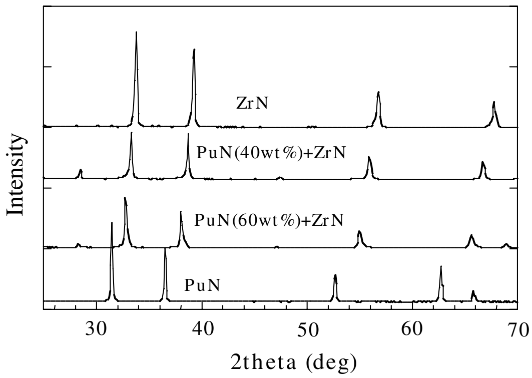

Fig. 7. X-ray diffraction patterns of (Pu, Zr)N, together with those of ZrN and PuN.

X-ray diffraction analysis was carried out to identify the phases and to determine the lattice parameters. To avoid the effect of the self-radiation damage accumulated in the lattice, the measurements were made immediately after cooling the heated sample for stoichiometry control. Fig. 7 shows the X-ray diffraction patterns of the pellets, together with those of ZrN and PuN [24]. The X-ray diffraction analysis revealed the formation of (Pu,Zr)N solid solution and the lattice parameters almost agreed with the values estimated from Vegard's law between PuN and ZrN.

Pellets of $(Pu_{0.1}Zr_{0.9})N$ were fabricated for an irradiation test in the Japan Materials Testing Reactor (JMTR). Fig. 8 shows $(Pu_{0.1}Zr_{0.9})N$ pellets for the irradiation test. These pellets, together with pellets of PuN + TiN, were enclosed in a He-bonded fuel pin. The characteristics of the $(Pu_{0.1}Zr_{0.9})N$ pellets are shown in Table 1 [26].

The irradiation test started in May 2002. It will go on for two years over 10 irradiation cycles in JMTR. After cooling for a few months, the post-irradiation examinations will be carried out at Reactor Fuel Examination Facility (RFEF) of JAERI in the half of 2004.

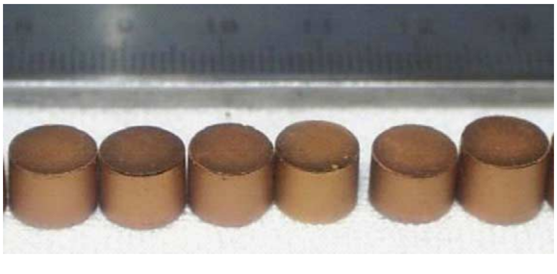

Fig. 8. (Pu,Zr)N pellets for irradiation test.

Table 1
Characteristics of (Pu,Zr)N and PuN + TiN pellets for irradiation test

Pellet	Composition	Pu content (wt%)	Density (%TD)	Chemical analysis		
				N (wt%)	O (wt%)	C (wt%)
(Pu, Zr)N	(Pu$_{0.1}$Zr$_{0.9}$)N	20	90	11.32	0.28	0.35
PuN + TiN	0.06PuN + 0.94TiN	20	87	14.42	0.79	0.50

3.4. PuN + TiN

PuN pellets containing TiN were fabricated by the classical mechanical blending method [24,25]. The procedure used was the same as that for the fabrication of (Pu, Zr)N pellets. Fig. 9 shows the X-ray diffraction patterns of the PuN pellets containing TiN, together with those of TiN and PuN [24]. The X-ray diffraction analysis revealed two separate phases of PuN and TiN with their lattice parameters unchanged, though TiN has the same structure of the face-centered cubic as PuN. A single phase is not a strict requirement for the fuel, but the control of microstructure becomes important if the fuel is a mixture of multi-phases.

The pellets of PuN + TiN were fabricated for the irradiation test in JMTR, as mentioned above. Fig. 10 shows the PuN + TiN pellets for the irradiation test. The characteristics of the PuN + TiN pellets are shown in Table 1.

4. Aspects of nitride fuel for transmutation

The mutual solubility among the actinide mononitrides is one of the important properties of the nitride fuel for the transmutation of MA. The amounts of each actinide nuclide to be transmuted would vary depending on the composition and irradiation history of the fuel in the power reactor fuel cycle as well as the recycle mode in the actinide burner cycle. This means that the transmutation fuel should accommodate a wide range of composition of actinides. The flexibility in the composition of the fuel could be achieved with the nitride fuel.

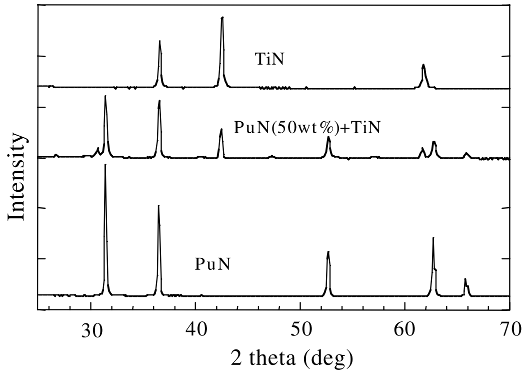

Fig. 9. X-ray diffraction pattern of PuN + TiN, together with those of TiN and PuN.

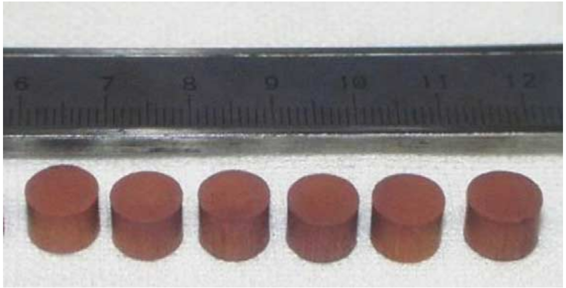

Fig. 10. PuN + TiN pellets for irradiation test.

In the case of UN, PuN and NpN, mutual solubility among them has been demonstrated as shown in Fig. 2. The solid solution of (Cm, Pu)N was also successfully synthesized. Table 2 compares the lattice parameters of mononitrides. Good mutual solubility among actinide mononitrides including AmN is expected from the small differences in lattice parameters, though experimental demonstration needs to be done.

For the transmutation fuel for the ADS core, the heavy metal content has to be diluted with an inert matrix. The criteria for the selection of the inert matrix are based on the physical and chemical properties, the irradiation performance and the feasibility for reprocessing. A high melting point and high thermal conductivity of the inert matrix are desirable and a good compatibility with the cladding and coolant is necessary. Irradiation stability of the inert matrix against neutrons, alpha particles and fission fragments is inevitable. The spent fuel in the actinide burner cycle has to be reprocessed.

As candidates for the inert matrix, YN, ZrN and TiN were examined. The mutual solubility of YN with AmN was demonstrated and good mutual solubility of YN with other actinides is expected from the small differences in lattice parameters, as shown in Table 2. In the pyrochemical reprocessing, YN dissolves easily in the molten salts. However, YN is highly hygroscopic.

Table 2
Lattice parameter differences between mononitrides

Mononitride	Lattice parameter a (nm)	Lattice parameter difference $\lvert a_{\mathrm{PuN}} - a \rvert$ (nm)	$\lvert a_{\mathrm{AmN}} - a \rvert$ (nm)
UN	0.4888	0.0017	0.0103
NpN	0.4899	0.0006	0.0092
PuN	0.4905	–	0.0086
AmN	0.4991	0.0086	–
CmN	0.5041	0.0136	0.0050
YN	0.4891	0.0014	0.0100
ZrN	0.4576	0.0329	0.0415
TiN	0.4242	0.0663	0.0749

The solid solutions of (Pu, Zr)N and (Am, Zr)N were obtained, but in the latter case the mixture of two solid solutions was obtained when the ratio Am/(Am + Zr) was 30 mol%. The drawback of ZrN as the inert matrix is that the dissolution of ZrN in the molten salts is difficult [3]. In the case of TiN, the solubility of PuN in TiN was very small and the mixture of PuN and TiN was obtained instead of the solid solution. Thus when TiN is used as the inert matrix, a composite fuel is obtained.

To date, few data are available on the irradiation performance and the applicability to the pyrochemical reprocessing of U-free inert matrix fuel. Although the irradiation experiment on the fuel pellets of (Pu,Zr)N and PuN + TiN is under way in JMTR, additional irradiation experiments on the fuel pellets containing minor actinides with inert matrix have to be made. An experiment on the pyrochemical process using the fuel pellets of (Pu, Zr)N and PuN + TiN will be started soon at JAERI. Along with these experiments, measurements of basic properties should be made on the nitride fuels containing MA with inert matrix.

5. Summary

At the JAERI, nitrides have been chosen as fuels candidates for the sub-critical core of the ADS to transmute minor actinides. MA nitrides, NpN, (Np, Pu)N, (Np, U)N, AmN and (Cm, Pu)N, and actinide nitrides with inert matrix, (Am, Y)N, (Am, Zr)N, (Pu, Zr)N and PuN + TiN, were prepared from the correspondent oxides by the carbothermic reduction method. The nitrides were examined by X-ray diffraction and the contents of impurities of carbon and oxygen were determined by combustion coulometry and inert gas fusion coulometry, respectively. For the irradiation test of U-free nitride fuels, pellets of (Pu, Zr)N and PuN + TiN were prepared and the irradiation test is under way.

The mutual solubility among UN, NpN and PuN, and between CmN and PuN were demonstrated. Good mutual solubility among actinide mononitrides including AmN is expected from the small differences in lattice parameters, though the experimental demonstration needs to be done. As candidates for the inert matrix, YN, ZrN and TiN were examined. Each material has its own advantages and disadvantages. The data are needed on the irradiation performance and the feasibility for the pyrochemical reprocessing of the inert matrix fuels. Along with the fabrication, irradiation and reprocessing experiments, measurements of basic properties should be made on the nitride fuels containing MA with inert matrix.

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