# NITRIDE FUEL AND PYROCHEMICAL PROCESS DEVELOPMENTS FOR TRANSMUTATION OF MINOR ACTINIDES IN JAERI

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## Abstract

The Japan Atomic Energy Research Institute (JAERI) has proposed the concept of the transmutation of minor actinides (MA: Np, Am and Cm) with accelerator-driven systems (ADS), where MA nitride is adopted as a fuel material of a sub-critical core, because nitride fuel has the advantage of accommodating various MAs with a wide range of composition besides superior thermal and neutronic properties. In this paper, the present status of study on fabrication, property measurements, irradiation test and pyrochemical process of nitride fuels in JAERI is presented.

**Introduction**

The Japan Atomic Energy Research Institute (JAERI) has proposed the double-strata fuel cycle for transmutation of long-lived minor actinides (MAs) such as Np, Am and Cm with accelerator-driven systems (ADS), where MA nitride is adopted as a fuel material of a sub-critical core [1]. The nitride fuel has been chosen as a candidate because of the possible mutual solubility among the actinide mononitrides and the excellent thermal properties besides supporting hard neutron spectrum. Highly enriched $^{15}$N would have to be used for the nitride fuel in order to prevent the formation of hazardous $^{14}$C. By applying pyrochemical process in the treatment of spent fuel, $^{15}$N could be readily recovered and recycled [2].

For the heterogeneous recycling of Am and Cm without U, solid solution or dispersed fuels, so-called U-free fuels, can be used in order to attain the requirements of the target for ADS such as chemical and physical stabilities at high temperature and high radiation dose. Nitrides containing MAs such as AmN[3], (Am,Y)N[4], (Am,Zr)N[4] and (Pu,Cm)N[5] have already been synthesized by the carbothermic reduction technique using their oxide powders as starting materials, where a carbon-rich condition was chosen from the properties that MA elements reduce the stability of carbides and increase the stability of oxides. On the other hand, spent fuel from ADS is treated by pyrochemical process, where MAs and Pu are recovered together in liquid cathode such as Cd [6, 7]. JAERI has also studied the pyrochemical process for nitride fuel cycle mainly by electrochemical measurements.

A five-year-program named *PROMINENT*, <u>pro</u>perty <u>m</u>easurements, pyrochemical process and <u>ir</u>radiation experiments <u>ne</u>eded for <u>ni</u>tride fuel <u>t</u>echnology, was also started in November 2002 within the framework of the Development of Innovative Nuclear Technologies by the Ministry of Education, Culture, Sports, Science and Technology of Japan. The purpose of the program is to clarify the feasibility of an innovative nuclear fuel cycle including minor actinides recycling based on the nitride fuel and pyrochemical reprocessing. In the program [8], the fuel fabrication and pyrochemical process technologies are developed and the fuel properties and irradiation behavior are studied for the MA-bearing fuels, as shown in Figure 1.

Figure 1. **Research areas in the program *PROMINENT***



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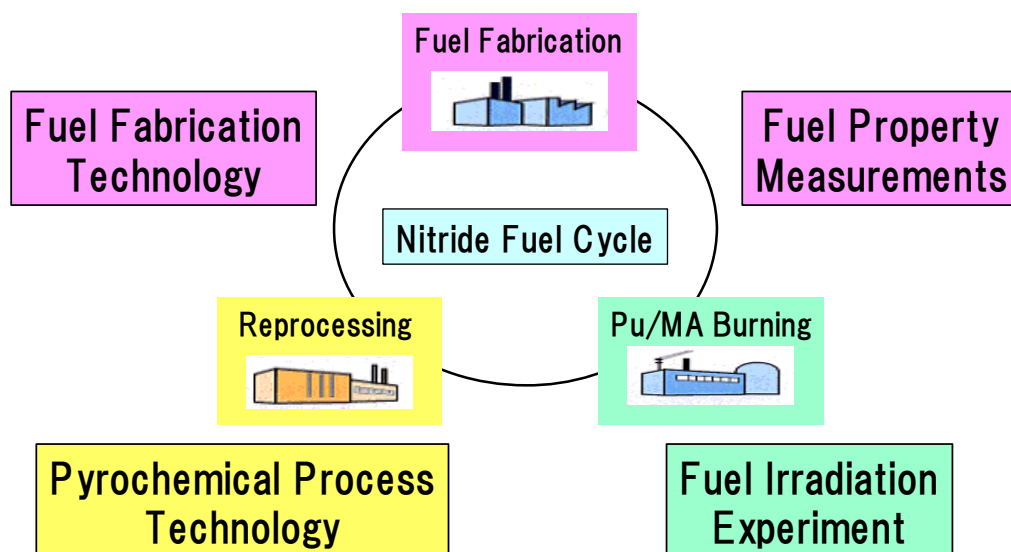
An inert atmosphere is necessary for handling of MA nitrides and other MA compounds such as chlorides. Within a collaborative program between JAERI and the Japan Atomic Power Company (JAPC), a new facility, called the Module for TRU High Temperature Chemistry (TRU-HITEC), has already been constructed in NUCEF (Nuclear Fuel Cycle Safety Engineering Facility). It consists of three hot cells shielded by steel and polyethylene and one glove box, where a high purity argon atmosphere is maintained. The limiting masses are 10 g of $^{241}$Am and 0.02 g of $^{244}$Cm. Many experimental apparatuses for MA fuels and pyrochemical reprocessing were installed in the cells and glove box [9].

## Fabrication of MA nitrides

### (Pu,Am,Cm)N and (Pu,Am,Cm,Zr)N

(Pu,Am,Cm)N and (Pu,Am,Cm,Zr)N were fabricated by the simultaneous carbothermic reduction of the respective oxide mixtures in approximately 40 mg scale. Powders of $^{243}$Am$_2$O$_3$, ($^{240}$Pu,$^{244}$Cm)O$_2$, ZrO$_2$ and amorphous carbon were used as starting materials. Compositions of the mixtures are summarized in Table 1. The C/M ratios shown are equivalent to about 200 and 130 % of the theoretically required carbon amounts for the reduction of each mixture, respectively.

Table 1. **Composition of TRU and zirconium oxide mixtures**

| Expected product | Pu/Am/Cm/Zr molar ratio | C/M molar ratio |
|---|---|---|
| (Pu,Am,Cm)N | 0.450 / 0.336 / 0.214 / 0 | 3.78 |
| (Pu,Am,Cm,Zr)N | 0.134 / 0.099 / 0.063 / 0.704 | 2.58 |

The mixtures were compacted into tablets with 4 mm in diameter by a pressure of 200 MPa. Then each tablet in a tungsten crucible was heated at 1523~1573 K in N$_2$ gas flow for nitridation. The carbothermic reduction reaction is formally represented by

$$MO_x + xC + 1/2N_2 \rightarrow MN + xCO. \qquad (1)$$

CO gas yielded by the reaction was monitored by infrared spectroscopy. After the CO gas release subsided, the temperature was raised up to 1773 K and the gas flow was replaced with N$_2$+4%H$_2$ for removal of the excess carbon. The decarburization was continued until the CO gas release subsided again. The CO gas release during the whole process is shown in Fig.2. For both samples, the temperature of 1523 K was regarded enough for nitridation from the CO gas release behavior.

X-ray diffraction with Cu-K$\alpha$ radiation was carried out to identify the phase of the products and to determine the lattice parameters. The lattice parameters of the nitrides increased with time after preparation because of the self-irradiation damage. The "undamaged" lattice parameters were estimated by extrapolating the lattice parameters to time=0. Nitrogen, oxygen and carbon contained in the products were also determined by chemical analyses.

Figure 2. **CO gas release during carbothermic reduction for the fabrication of (a) (Pu,Am,Cm,)N and (b) (Pu,Am,Cm,Zr)N**
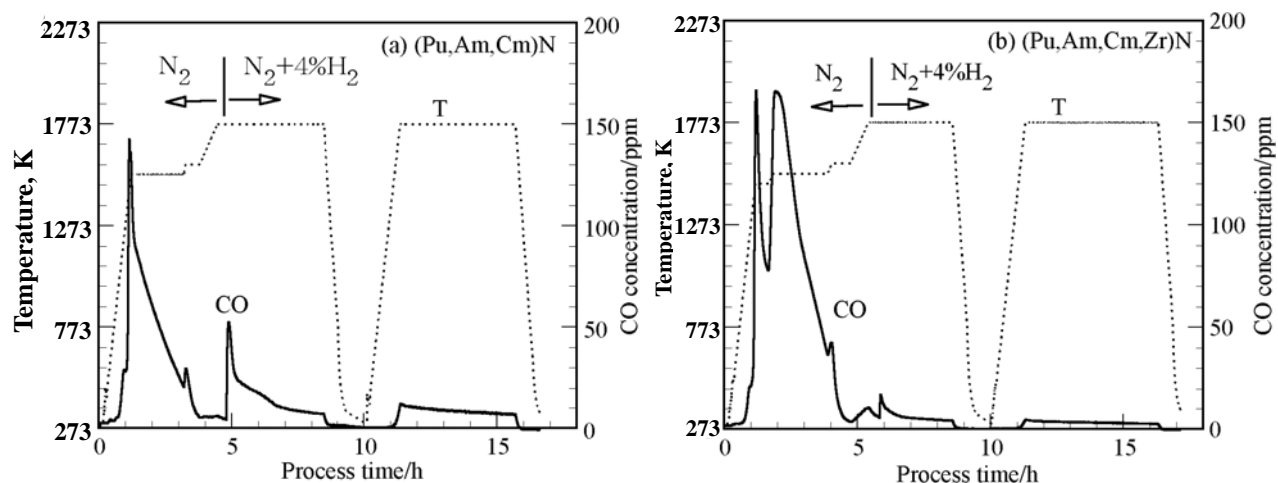


X-ray diffraction profiles of (Pu,Am,Cm)N and (Pu,Am,Cm,Zr)N are shown in Fig.3. (Pu,Am,Cm)N was single phase with NaCl-type structure, and any oxide phases were not recognized. The undamaged lattice parameter was 0.4956 nm, which agreed reasonably with 0.4960 nm calculated by Vegard's law using the values for PuN, AmN and CmN. The residual carbon content was less than 0.05 wt%. The low carbon content means the excess carbon was successfully removed in $N_2+4\%H_2$ mixed gas flow at 1773 K. On the other hand, the product containing zirconium consisted of two phases with NaCl-type structure. Oxygen and carbon contents were 0.15 and 1.31 wt%, respectively. The high carbon content suggests that the excess carbon remained as carbonitride. It is known that ZrN can form carbonitride, $Zr(N_{1-x}C_x)$, with a wide range of $x$ values. Judging from the calculated peak positions of the constituent nitrides and ZrC shown in the figure, these two phases are considered to be solid solutions with different (Pu+Am+Cm)/Zr ratios. The factors affecting the mutual solubility among TRU nitrides and ZrN fabricated by the carbothermic reduction should be studied further.

Figure 3. **X-ray diffraction profiles of (Pu,Am,Cm)N and (Pu,Am,Cm,Zr)N**



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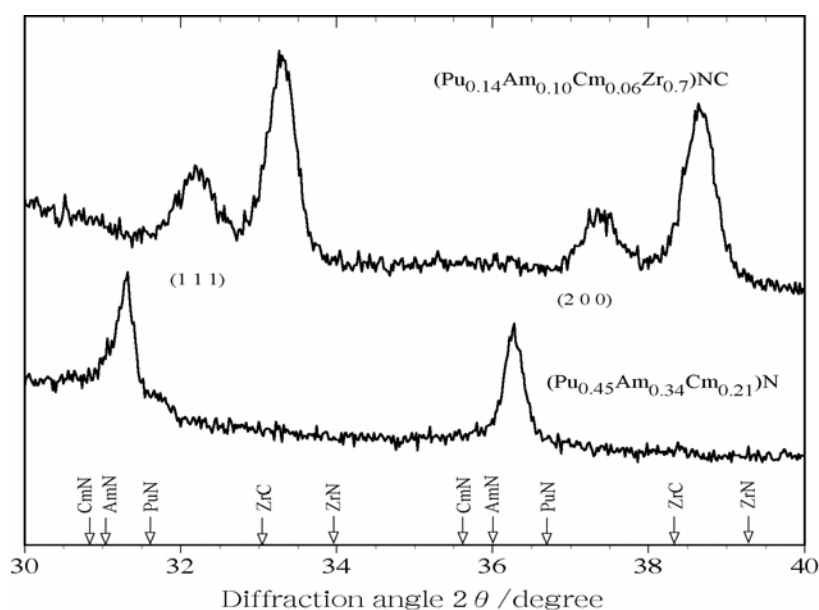
**Property Measurements of MA nitrides**

*Hydrolytic behaviour*

Hydrolytic behaviour of Am-based nitrides, AmN and (Am,Zr)N solid solution, was investigated by measuring the weight change in ambient air. The weight gains are shown in Fig.4 as a function of exposure time in air. The weight gain of AmN was rapid compared with that of (Am,Zr)N and saturated within 20 hours. The volume increase during exposure to air was considerably large, and the color of AmN changed from black into light brown. From the weight gain and the chemical analysis of C,N and O before and behind the exposure, the main product was considered to be a hydroxide, $Am(OH)_3$. The high carbon content of 0.3 – 2 wt% in the reacted AmN suggests that a part of $Am(OH)_3$ reacted with $CO_2$ in the atmosphere to form a hydrooxy-cabonate, $AmOHCO_3$ and/or a carbonate, $Am_2(CO_3)_3$.

Figure 4. **Weight gains of AmN and (Am,Zr)N in air**
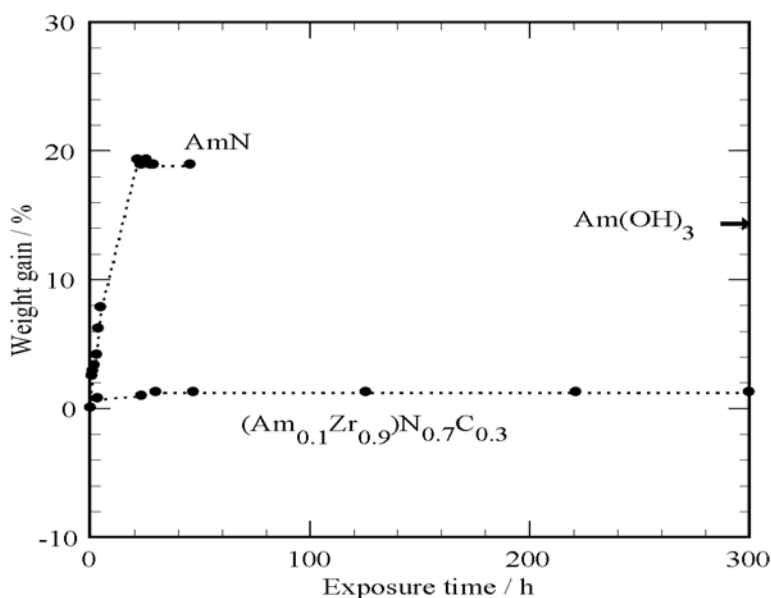


For the solid solution of $(Am_{0.1}Zr_{0.9})N$, the weight gain was very small compared with that of AmN, and remained constant at about 1.5 % after 1000 hours. From XRD measurement of the resulted sample, (Am,Zr)N solid solution retained the structure after the long-time exposure in air. Therefore, the result suggested that AmN was significantly stabilized against moisture by the formation of solid solution with ZrN.

*Evaporation behaviour*

Evaporation behaviour of AmN and (Am,Zr)N solid solution in He gas flow was investigated by measuring $N_2$ release with a gas chromatography. For AmN, nitrogen release was detected above about 1570 K, and large weight loss was found after heating. However, AmN retained the structure after heating and the metallic phase was not found. For (Am,Zr)N solid solution, the mole fraction of Am/(Am+Zr) decreased from 0.1 to 0.03. The result suggests that selective vaporization of AmN on (Am,Zr)N solid solution occurred.

Figure 5 shows the evaporation behaviour of AmN and (Am,Zr)N as a function of temperature, where the evaporation rate constant (1/s) is defined from the evaporation rate (mol/s) and the amount of remained AmN (mol). A linear relationship between log (Evaporation rate const.) and reciprocal temperature was clearly found in AmN, but not in (Am,Zr)N. The non-linear relationship for (Am,Zr)N is thought to be mainly due to the decrease of AmN fraction in (Am,Zr)N during heating. It was also found that the addition of ZrN into AmN depressed the vaporisation of Am on the nitride.

Figure 5. **Arrhenius plots of the evaporation rate constants for AmN and $(Am_{0.1}Zr_{0.9})N_{0.85}C_{0.15}$**
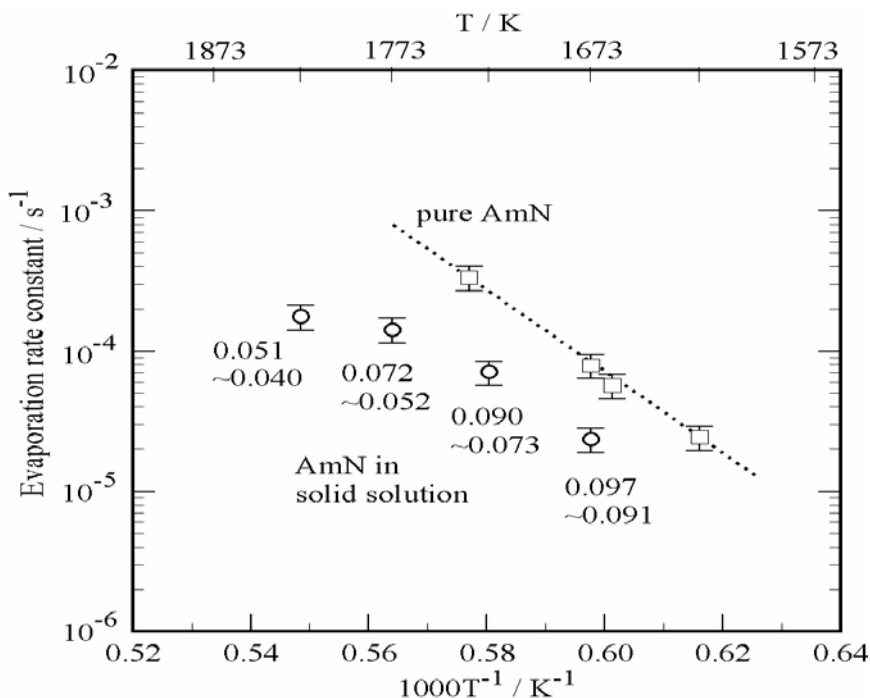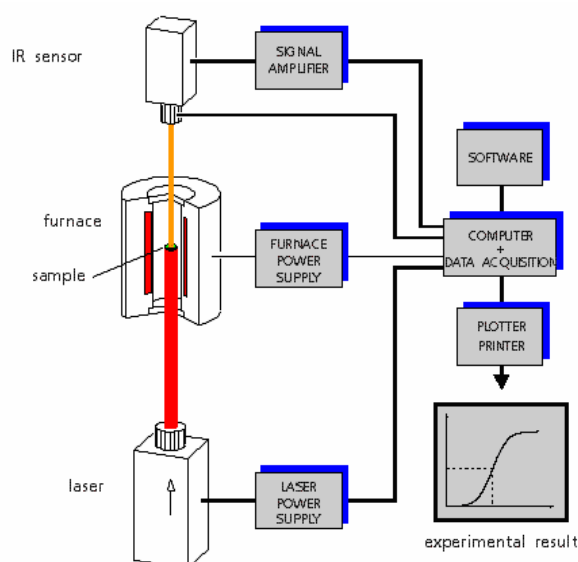


*New experimental apparatuses*

For the purpose of measuring thermal properties such as thermal diffusivity and specific heat capacity of MA nitrides, two experimental equipments were newly installed in WASTEF (Waste Safety Testing Facility). The thermal diffusivity measuring equipment based on laser flash method was specially designed to make measuring small samples of MA nitrides and handling the samples in an inert atmosphere possible. The specific heat capacity measuring equipment based on drop calorimetry method was also installed in an air-atmosphered glove box. Figure 6 shows schematic diagrams of the new experimental apparatuses.

Figure 6. **Schematic diagrams of newly installed experimental apparatuses**

(a) thermal diffusivity measurement  (b) specific heat capacity measurement
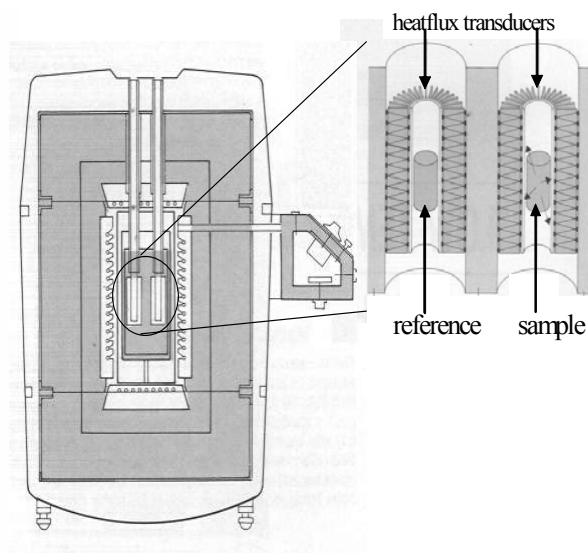


## Pyrochemical process

### *Renitridation of Pu in Pu-Cd melt by nitridation-distillation combined process*

For renitridation of Pu in Pu-Cd melt, two processes, which are $N_2$ gas bubbling process and nitridation-distillation combined process, were examined. Figure 7 shows the schematic diagrams of renitridation processes of Pu in Pu-Cd melt. In the bubbling process, LiCl-KCl eutectic salt was used to prevent the evaporation of Cd. However, the renitridation of Pu in Pu-Cd melt at 723 K proceeded very slowly and a large part of Pu remained in the melt. This result was mainly due to very small activity coefficient of Pu in the melt.

On the other hand, in the combined process, in order to enhance the activity of Pu in Pu-Cd melt, two processes, which were the distillation of Cd from Pu-Cd melt and the nitridation of Pu, were combined and practiced simultaneously. The experiment was carried out at 973K using an apparatus shown in Fig.7. Pu content of the sample used for this test was 12wt%. Almost all of Pu was converted to plutonium nitride (PuN) of high purity, which was confirmed by the X-ray diffraction measurement of recovered material. As a result, the nitridation-distillation combined process is very useful and very simple because PuN powder can be obtained by a single process.

Figure 7. **Schematic diagrams of renitridation processes of Pu in Pu-Cd melt**

(a) $N_2$ bubbling process
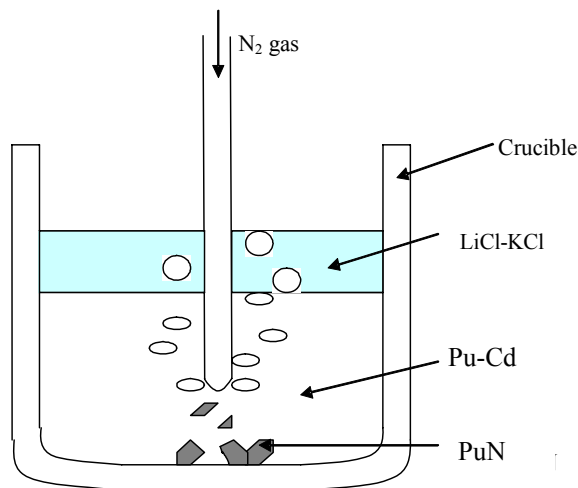
(b) nitridation-distillation combined process
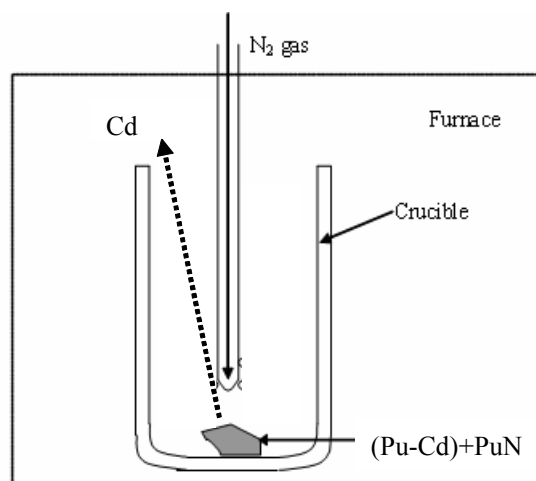


### Irradiation test of nitride fuels

The irradiation test of a He-bonded fuel pin containing (Pu,Zr)N and PuN+TiN pellets of 20wt% in Pu contents was started in May 2002 at JMTR (Japan Materials Testing Reactor) [10]. The irradiation is now in progress. Up to the present, it seems that the fuel pin remains intact, where the average linear powers were estimated to be 41 and 36 kW/m for (Pu,Zr)N and (PuN+TiN), respectively. It is also expected that the burn-ups are less than 16 and 20 at% of Pu scheduled, respectively. After one more cycle of irradiation and cooling for a few months, the post-irradiation examination is planned at RFEF (Reactor Fuel Examination Facility) from April, next year.

### Concluding remarks

The present status of study on fabrication, property measurement, pyrochemical process and irradiation test of nitride fuels in JAERI are summarized.

(Pu,Am,Cm)N and (Pu,Am,Cm,Zr)N were prepared by the carbothermic reduction method. The solid solution of (Pu,Am,Cm)N was successfully prepared to demonstrate the mutual solubility.

Chemical and thermochemical stability of AmN and (Am,Zr)N was studied in terms of the hydrolysis behavior at room temperature and the evaporation behavior at elevated temperatures. In both the cases AmN was stabilized by the formation of solid solution with ZrN. Thermal properties such as thermal diffusivity, specific heat capacity etc. will be measured.

Nitride formation behavior of Pu-Cd alloy was experimentally investigated. Heating of Pu-Cd alloy at 973 K in $N_2$ stream resulted in almost complete nitride formation of Pu and distillation of Cd simultaneously.

The irradiation test of a fuel pin containing (Pu,Zr)N and PuN+TiN pellets is in progress in JMTR, followed by post-irradiation examinations in 2005.

**Acknowledgement**

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