Fabrication and electrochemical behavior of nitride fuel for future applications

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Abstract

Mononitride is the first candidate of fuel material in the accelerator driven system (ADS) for minor actinide (MA) transmutation designed by JAERI, being coupled with pyrochemical process for treatment of spent fuel. This paper summarizes recent R&D on the fabrication and electrochemical behavior of nitride fuel carried out in JAERI. Mononitride of U, Np, Pu, Am, Cm and their solid solutions have been prepared by carbothermic reduction from their dioxides. Mononitride containing diluent material such as ZrN also has been prepared and characterized. Electrode behavior of nitride fuel in the LiCl–KCl eutectic melt has been investigated by electrochemical measurements in order to apply pyrochemical process to nitride fuel cycle for MA transmutation.
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1. Introduction

Actinide mononitride has been considered as an advanced fuel for fast reactors since 1970s because of superior thermal and neutronic properties. Recently R&D on nitride fuel has been expanded to MA transmutation system represented by subcritical ADS. Probable mutual solubility among actinide mononitrides becomes an important advantage for the fuel containing MA as a primary component. Accordingly, JAERI has carried out the fundamental research on nitride fuel for more than a decade, which includes fabrication technology, thermochemical property, irradiation behavior and so

on. However, the experimental database of nitride fuel has not been sufficient for technological development at present, especially for MA bearing nitrides. Another important subject is the treatment of spent fuel. It is well known that pyrochemical process has several advantages over conventional wet process for treating spent fuel with high radiation dose and decay heat. Especially for nitride fuel with N-15 enriched nitrogen, the recovery of expensive N-15 seems technologically feasible in case of pyrochemical process. JAERI has also studied pyrochemical process for nitride fuel cycle mainly by electrochemical measurements.

There are two excellent texts for nitride fuel cycle, one was written by Matzke in 1986 [1] and the other by Blank in 1994 [2]. They described all aspects of nitride fuel, from basic property to irradiation behavior, along with those of preceded carbide fuel having many similar characteristics. Results on fundamental research carried

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out in European Institute for Transuranium Elements (ITU) to 1980s were reflected in the contents. On the other hand, a review paper was reported from JAERI in the latter half of 1990s, in which Suzuki et al. summarized thermodynamic and thermochemical properties of nitride fuel including the results obtained by JAERI [3]. This paper summarizes recent JAERI's R&D on fabrication and electrochemical behavior of nitride fuel for MA transmutation after the review by Suzuki et al.

2. Fabrication of nitride fuel

2.1. Carbothermic reduction

Actinide mononitrides, UN, NpN, PuN, AmN, CmN and their solid solutions were prepared by carbothermic reduction from their dioxide [4–8]. Carbothermic reduction consists of two processes in general, the conversion of dioxide to carbonitride by heating the mixture of dioxide and carbon in N_2 gas flow, followed by the removal of residual carbon by heating in N_2–H_2 mixed gas flow. Main attention has been paid to lowering oxygen and carbon impurities in the products and suppressing loss of actinide due to evaporation.

Equilibrium of carbothermic reduction indicated in Eq. (1) is related to phase relations of An–N–C–O system (An: actinide element) and partial pressures of $N_2(g)$, $CO(g)$, and $An(g)$ as well as carbon activity [9],

$$AnO_2(s) + 2C(s) + 0.5N_2(g) = AnN(s) + 2CO(g) \quad (1)$$
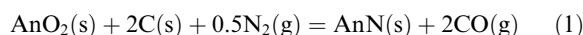
Normally, an excess amount of carbon over stoichiometric value of 2.0 is added to the dioxide in carbothermic reduction. Compared with lighter actinides, heavier actinides have less thermodynamic stability of carbides but high thermodynamic stability of oxides [10,11]. So the amount of excess carbon added should be adjusted elements by element so as to prepare mononitride with high purity. Table 1 shows the composition of carbonitride obtained by heating the two-phase mixture of carbonitride and free carbon at 1823 K in N_2 atmosphere, which was estimated by the lattice parameter and chemical analysis, in comparison with the calculated results based on thermodynamic equilibrium in literatures including a few assumptions [12–15]. The experimental

and calculated values almost agree with each other and the carbon content in carbonitride phase decreases with U, Np and Pu in order. Lack of thermodynamic values misses the similar calculation for Am and Cm. It is expected that the residual carbon tends to form carbonitride in lighter actinides but to exist in elementary state in heavier actinides. Since the removal of carbon in carbonitride is difficult compared with that of free carbon from kinetic reason, the amount of excess carbon is empirically adjusted to 2.2–2.5 in lighter actinides and more than 3.0 in heavier actinides. In that case, besides the carbon impurity, the oxygen impurity in mononitrides is lowered to less than 0.1 wt%, including the case of AmN prepared by the following manner.

Loss of actinide due to evaporation practically becomes a problem in case of preparation of AmN, where partial pressure of $CO(g)$ during carbothermic reduction is low due to high thermodynamic stability of Am_2O_3 and partial pressure of $Am(g)$ becomes high with increasing temperature [9]. So the temperature of carbothermic reduction is lowered by about 200 K compared with the other cases in JAERI. Carbothermic reduction at 1573 K with the molar mixing ratio of C/AmO_2 higher than 3.0 resulted in the formation of high-purity AmN without significant loss of Am [7].

Kinetics of carbothermic reduction becomes important for technological preparation of nitride fuel. Results of thermogravimetry indicated carbothermic reduction obeys with the first order rate equation and the reaction rate is controlled by a solid-state diffusion process across the product layer [16–18]. So it is reasonable to use fine powders of dioxide and carbon. On the other hand, the result of thermogravimetry for removal of excess carbon indicated that the reaction apparently obeys with phase boundary equation [18]. However, it should be noted that the result includes both removal of free carbon and substitution of carbon by nitrogen in carbonitride causing opposite weight changes.

2.2. Formation of solid solution

Dedicated fuel for MA transmutation should accommodate a wide range of composition, since the amounts of actinide nuclide to be transmuted depends on the irradiation history in commercial fuel cycle as well as the recycle mode of MA transmutation. Flexibility of the composition could be achieved in nitride fuel with mutual solubility among actinide mononitrides. This characteristic is derived from the similar bonding nature and lattice parameters in U, Np, Pu, Am and Cm mononitrides, besides absence of higher nitrides except for U_2N_3 and UN_{2-x}.

Single-phase solid solutions of (U,Np)N, (Np,Pu)N, (Pu,Cm)N as well as (U,Pu)N have been prepared by direct carbothermic reduction of mixture of dioxides

Table 1
Equilibrium composition of U, Np and Pu carbonitride coexisting with free carbon at 1823 K under $P_{N_2}(g) = 0.1$ MPa

	x in $U(C_{1-x}N_x)$	x in $Np(C_{1-x}N_x)$	x in $Pu(C_{1-x}N_x)$
Experimental results	0.86	0.96	0.99
Calculated results	0.85	0.96	>0.99

or heating the mixture of each nitride mechanically blended [5,8,19]. Lattice parameters of the solid solution show a small deviation from the value calculated from the Vegard's law. Recently $(Pu_{0.45}Am_{0.34}Cm_{0.21})N$ has been prepared by carbothermic reduction of $(Pu,Cm)O_2$ and AmO_2 mixtures. The X-ray diffraction pattern showed the formation of solid solution with an almost single phase [20].

U-free nitride fuel used in ADS should contain diluent materials such as ZrN, YN and TiN. These nitrides have the NaCl-type structure as actinide mononitride and their lattice parameters are shown in Table 2 along with those of actinide mononitride. So far the solid solutions of $(Pu_xZr_{1-x})N$ ($x = 0.23$ and 0.42), $(Am_{0.10}Zr_{0.90})N$, $(Am_xY_{1-x})N$ ($x = 0.09$, 0.20 and 0.31) have been prepared and characterized [21,22]. On the other hand, it was found that the mixed nitride corresponding to $(Am_{0.30}Zr_{0.70})N$ consisted of two NaCl-type phases with different Am and Zr contents as shown in Fig. 1 [22]. The solubility of PuN and TiN proved to

be negligibly small under the experimental condition [21]. Benedict has presumed the solubility of solid fission products in carbide and nitride fuel based on the relative lattice parameter difference indicated as RLPD in Table 2 [23]. The present experimental results qualitatively agree with the presumption of Benedict, who claimed the complete solubility in case of $-7.5\% <$ RLPD $< +8.5\%$. For AmN-ZrN system, RLPD is calculated at -8.3%. Another possible reason of existing two NaCl-type phases in $(Am_{0.3}Zr_{0.7})N$ is high residual carbon content of 0.7 wt% in the sample. Carbon likely remains as carbonitride in Zr bearing nitride prepared by carbothermic reduction because of high thermodynamic stability of ZrC. It is probable that one carbonitride phase with high carbon content has Zr-rich composition and the other with low carbon content has Am-rich composition, and they are not dissolved with each other.

2.3. Sintering

The density of nitride fuel pellet for MA transmutation has not been optimized yet for the moment. However, 80%TD will be necessary at least for keeping geometrical integrity and confining fission products during irradiation. Nitride fuel is known to be hard to sinter compared with oxide fuel due to slow isothermal diffusion of heavy metal at sintering temperature. For (U,Pu)N or (Pu,Zr)N pellets, dense pellets higher than 90%TD were obtained by grinding powder for a long time and sintering green pellets at temperature higher than 1973 K [4,21]. However, in case of Am-bearing nitride pellets, high sintering temperature results in loss of Am due to evaporation. Partial pressures of U(g), Np(g), Pu(g) and Am(g) over mononitrides are shown in Fig. 2, which was calculated from the results of vapor

Table 2
Lattice parameters of ZrN, YN, TiN and actinide mononitride

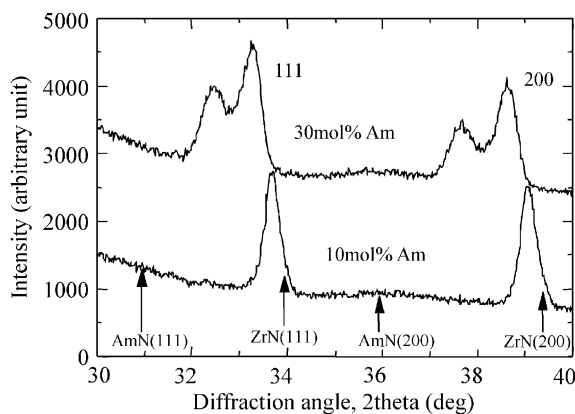|	Lattice parameter (nm)	RLPD[a]	
	a	$(a - a_{PuN})/a_{PuN}$, %	$(a - a_{AmN})/a_{AmN}$, %
TiN	0.4242	−13.5	−15.0
ZrN	0.4576	−6.7	−8.3
YN	0.4891	−0.3	−2.0
UN	0.4888	−0.3	−2.1
NpN	0.4899	−0.1	−1.8
PuN	0.4905	–	−1.7
AmN	0.4991	+1.8	–
CmN	0.5041	+2.8	+1.0

[a] Relative lattice parameter difference.

Fig. 1. X-ray diffraction patterns of (Am,Zr)N containing 30 mol% (upper) and 10 mol% (lower) of Am.
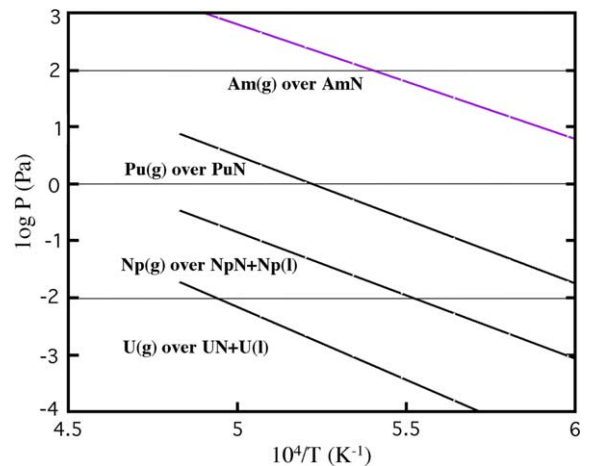

Fig. 2. Temperature dependence of partial pressures of U(g), Np(g), Pu(g) and Am(g) over mononitrides.

pressure measurements over UN, NpN and PuN containing a small amount of Am [15,24,25]. It is seen that partial pressure of Am(g) over AmN is higher than that of Pu(g) over PuN by about three orders. Recent US results on sintering $(Am_{0.24}Pu_{0.16}Zr_{0.60})N$ pellets in Ar gas flow showed a significant loss of Am and the similar phenomena could be reproduced by thermodynamic and kinetic models by Jolkkonen et al. [26]. They concluded that sintering in N_2 or N_2–H_2 atmosphere is indispensable for Am-bearing nitrides.

However, sintering experiments of (U,Pu)N and (Pu,Zr)N in JAERI suggest that the pellets sintered in N_2–H_2 atmosphere tend to have a lower density than those sintered in Ar or Ar–H_2 atmosphere. The reason has not been clarified yet, but probable formation of nitrogen vacancy produced by sintering in Ar or Ar–H_2 atmosphere may accelerate the diffusion of heavy metal in nitride fuel. Although the difference in chemical composition was not confirmed, difference in grain size was seen between (U,Pu)N pellets sintered in N_2–H_2 and Ar or Ar–H_2 atmospheres [4]. Screening test of sintering aid for nitride fuel is planned in JAERI in order to fabricate dense pellets by sintering in N_2 or N_2–H_2 atmosphere at temperature lower than 1773 K.

3. Electrochemical property of nitride fuel in LiCl–KCl melt

Pyrochemical treatment of spent nitride fuel for MA transmutation consists of anodic dissolution in the LiCl–KCl eutectic melt, recovery of Pu and MA into liquid Cd cathode and nitride formation of Pu and MA in liquid Cd, besides relating technologies such as off gas treatment and salt waste treatment.

3.1. Anodic reactions

Anodic dissolution of actinide mononitride is indicated by Eq. (2)

$$AnN(s) = An^{3+} + 3e^- + 0.5N_2(g) \qquad (2)$$
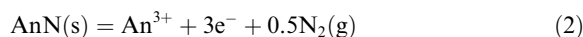
Electrode reactions of Eq. (2) were investigated by cyclic voltammetry and electromotive force measurements mainly at 773 K [27–29]. Further, evolved nitrogen gas was analyzed by gas chromatography. Equilibrium potential of AnN in the LiCl–KCl melt, E vs. the Ag/AgCl reference electrode, can be represented by Eq. (3),

$$E = E_{An^{3+}/An\text{-}Ag/AgCl} - G^\circ_{f(AnN)}/3F + (RT)/(6F)\ln p_{N_2}, \qquad (3)$$

where $E_{An^{3+}/An\text{-}Ag/AgCl}$ is the redox potential of An^{3+}/An vs. the Ag/AgCl reference electrode, $G^\circ_{f(AnN)}$ the free energy of formation of AnN, p_{N_2} the partial pressure of $N_2(g)$ in the melt and F the Faraday constant. Deter-
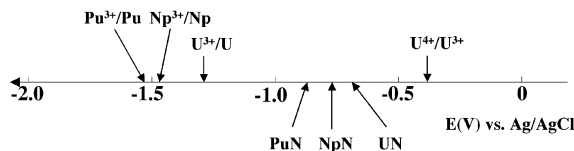

Fig. 3. Equilibrium potentials of An(III)/An(0) couple in the LiCl–KCl melt and potential shift by formation of mononitride.

mined equilibrium potentials of UN, NpN and PuN and relations with the redox potentials of U^{3+}/U, Np^{3+}/Np and Pu^{3+}/Pu couples are shown in Fig. 3. It is seen that the equilibrium potentials of AnN are shifted positively by about 0.7 V compared with redox potential of An^{3+}/An and this potential shift is similar with the case of rare earth elements. Further, U^{4+}/U^{3+} reaction is found in anodic dissolution of UN at more positive potential than -0.45 V vs. the Ag/AgCl [29]. Oxidation of U^{3+} to U^{4+} in the melt leads to formation and precipitation of UNCl, which deteriorates the efficiency of electrorefining. However, no formation of NpNCl or PuNCl was observed in anodic dissolution of NpN and PuN under the experimental condition due to relative high stability of Np^{3+} and Pu^{3+} in the melt.

3.2. Cathodic reactions

Recovery of actinides into liquid Cd cathode has been investigated in JAERI under the joint research with CRIEPI (Central Research Institute of Electric Power Industry). It has been demonstrated that Pu is smoothly recovered into liquid Cd cathode with high current efficiency by electrorefining of the LiCl–KCl–PuCl₃ melt at 773 K [30]. Since the amount of Pu recovered exceeds the solubility limit of Pu in liquid Cd, Pu–Cd binary alloy is formed besides Pu-saturated liquid Cd phase. The binary alloy was identified to be $PuCd_6$ by electron probe microanalysis at room temperature. It was also found that a small amount of Am existing in Pu almost similarly behaved with Pu.

Nitride formation behavior of Pu in Pu–Cd alloy was investigated. Previous literatures reported successful nitridation of U dissolved in liquid Cd by passing N_2 gas through the liquid phase at 773–873 K [31,32]. However, it proved that Pu dissolved in liquid Cd was not converted to nitride in the same manner because of high thermodynamic stability of Pu in liquid Cd phase. Although the free energies of formation for UN and PuN are almost similar at 773 K, the activity coefficient of Pu in liquid Cd phase is lower than that of U by more than five orders. So the nitridation of Pu in Pu–Cd alloy was investigated by nitridation–distillation combined method using the alloy containing Pu of 12 wt% [33]. This process aims at proceeding with nitridation of Pu in Pu–Cd alloy and distillation of Cd simultaneously.

By heating Pu–Cd alloy in N_2 gas atmosphere at 973 K, most of Pu was recovered as PuN powder, while most of Cd was evaporated to condensed part.

4. Conclusion

Actinide mononitrides and their solid solutions were prepared by carbothermic reduction in N_2 and subsequently N_2–H_2 mixed gas stream. The impurity contents of oxygen and carbon could be lowered to less than 0.1 wt% by adjusting mixing carbon to dioxide ratio and the evaporation of actinides was controlled by lowering reduction temperature in case of Am bearing nitrides. Formation of solid solution with diluent material such as (Pu,Zr)N, (Am,Y)N and $(Am_{0.1}Zr_{0.9})N$ was confirmed but the XRD pattern for $(Am_{0.3}Zr_{0.7})N$ showed two NaCl-type phases with different Am and Zr composition. For nitride fuel for MA transmutation, sintering in N_2 or N_2–H_2 atmosphere at temperature lower than 1773 K is preferred for suppressing significant loss of Am. Further study is needed for fabricating dense pellets under these conditions.

Electrode reaction of actinide mononitride has been examined mainly by electrochemical measurements. Anodic dissolution in the LiCl–KCl melt was investigated by cyclic voltammetry and the equilibrium potentials were determined by electromotive force measurements. Recovery of Pu into liquid Cd cathode by electrorefining was demonstrated in a laboratory scale with high current efficiency. Nitride formation of Pu in Pu–Cd alloy was developed by use of nitridation–distillation combined method. Most of Pu in Pu–Cd alloy was converted to nitride and recovered as PuN powder with high purity.

Five-years R&D program PROMINENT (Property measurements, pyrochemical process and irradiation experiments needed for nitride fuel cycle technology) was started in 2002 within the framework of the Development of Innovative Nuclear Technologies by the Ministry of Education, Culture, Sports, Science and Technology of Japan. JAERI is in charge of implementing the program with the aid of domestic and international collaborations. This paper contains some results obtained in the program and further study will be carried out in the program mainly focusing on MA bearing nitrides.

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