

STUDIES ON NITRIDE FUEL CYCLE FOR TRU BURNING

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The research on a nitride fuel cycle for burning transuranium elements (TRUs) in actinide burning reactors (ABR) has been carried out in JAERI. With regard to fuel fabrication, the techniques of direct conversion of actinide nitrate solution from the reprocessing to nitride have been studied by applying the sol-gel method. It was confirmed that pure neptunium mononitride can be prepared by carbothermic reduction of the dioxide. The CVD process is also being developed for coating low density TiN to nitride fuel particles. The properties necessary for fuel design were investigated by using the samples synthesized by carbothermic reduction. The thermal conductivity of NpN was estimated from the thermal diffusivity determined by a laser-flash method. The partial pressures of Np and Am over the nitrides were measured by Knudsen-effusion mass spectrometry. The status of the research on the pyro-chemical process with fused salt electrorefining is also described.

1. Introduction

Nitride fuel will enable the adoption of the cold fuel concept, because of its good thermal properties, which result in lower fuel temperature and hence lower fission gas release. Furthermore, the cold fuel may accept a thinner cladding and make the neutron spectrum harder. The mutual miscibility of actinide mononitrides also leads to the fuel design of high concentration of transuranium elements (TRUs). Actinide burner reactor (ABR) concepts with Na-bonded pelletized fuel and TiN-coated particle fuel have been proposed from JAERI [1], based on the excellent thermal characteristics of actinide nitrides. For reprocessing, an innovative fuel cycle combined with fused salt electrorefining will be available in the case of nitride fuel as well as metallic fuel [2].

Fabrication method of TRU nitride fuel and their properties have been studied in JAERI following the concept of the transmutation of TRUs at ABR. In the present paper, the status of the research on nitride fuel for TRU burning is described.

2. Fabrication of fuels for TRU burning

2.1 Sol-gel method

Synthesis of the nitrides can be made by carbothermic reduction of the oxides in a nitrogen atmosphere. Minor actinides (Np, Am and Cm) will be separated from the high-level waste as nitrates. The actinide nitrates will then be converted to the mixture of oxides and carbon via the sol-gel techniques, which is to be fed to the carbothermic synthesis of the nitrides.

The sol-gel process is studied with particular emphasis on the application of microwave techniques first introduced by PSI, Switzerland[3]. The process is basically the internal gelation process. The ammonia donor, HMTA(hexamethylenetetramine), is added to the nitrate solution. By heating the liquid droplets to $\sim 80^{\circ}\text{C}$, HMTA is decomposed to form ammonia. The heating of the droplets by microwave is almost spontaneous: gelling of droplets is complete while they fall through a microwave cavity of ~ 20 mm length(fig. 1). In our apparatus, an industrial frequency of 2.45 GHz has been successfully employed for the gelling of uranium nitrate solution[4]. Further efforts are being made:

- (1)Mixing of the feed solution right above the nozzle in order to prevent the premature gelling by alpha-decay heat.
- (2)Designing microwave cavity to minimize the droplet falling distance.

2.2 Preparation of neptunium nitride by carbothermic reduction

Actinide nitrides such as UN and PuN can be synthesized by carbothermic reduction of the dioxides with graphite in a $\text{N}_2\text{-H}_2$ mixed gas stream[5,6]. The same techniques were applied to the preparation of the mononitride of Np-237 from the dioxide[7]. The mixture of NpO_2 and graphite with a C/Np ratio of 2.2 was compacted into thin discs of 12 mm in diameter and about 2 mm in height. The compacts were first heated at 1,823 K in a N_2 stream for 36 ks to convert oxide to nitride and then heated at 1,723 K in $\text{N}_2\text{-8\%H}_2$ for removing residual carbon in nitride.

The product was confirmed by X-ray analysis to be a nearly single phase with NaCl-type structure having the lattice parameter of 0.48968 ± 0.00006 nm, which is close to the value of the mononitride prepared by hydriding-nitriding of the metal, 0.48979 ± 0.00003 nm[8] and 0.48987 ± 0.00005 nm[9]. Chemical analysis of the product[10,11] revealed that the impurity contents of carbon and oxygen are low as shown in table 1. It is shown from the result that NpO_2 could be converted to pure NpN by a similar procedure to the cases of UN and PuN.

It is notified from the experience of nitride fuel fabrication that residual carbon contents in actinide mononitrides synthesized by carbothermic reduction have a tendency to decrease with increasing atomic number. It could be explained from thermodynamic estimation that the removability of carbon depends on the solubility of carbon in nitride phase. In the case of UN, the solubility of carbon in the nitride phase is calculated to be around 0.10 at 1,723 K. On the other hand, the solubility of carbon in PuN is below 0.01. Such differences in carbon solubility may affect the content of residual carbon in UN, NpN and PuN.

The mononitride synthesized from the oxide was ground and compacted into a green pellet, which was heated at 2,000 K for 72 ks in a $\text{N}_2\text{-8\%H}_2$ atmosphere. The sintered density reached over 90 % of theoretical density(T.D.). Sample preparation was carried out in gloveboxes filled with purified argon gas[12]. The oxygen and water levels of the atmosphere in the gloveboxes were less than 3 and 5 ppm, respectively. The NpN sample prepared was supplied for the studies on the properties such as thermal conductivity and vapor pressure as described below.

2.3 CVD coating of TiN

One of the burner concepts employs the TiN-coated fuel particles whose surface is directly cooled by helium. The design permits the use of the cold fuel concept where the fuel temperature is kept below 1,000 K, that is, $\sim 1/3$ of the melting point of the fuel nitrides. The coating is of a duplex type: the fuel kernel is coated with low-density and high-density TiN layers. The inner low-density layer acts as a buffer to prevent the outer high-density layer from the fission recoil damage.

In JAERI, techniques for the CVD coating of the refractory ceramics such as ZrC have been developed within the high-temperature gas-cooled reactor program[13]. The techniques will be readily applied for the TiN coating. Besides, there is a range of industrial application of CVD-TiN such as a coating for cutting tools. However, there have been little experience in the CVD synthesis of the low-density TiN.

In order to demonstrate the feasibility of the CVD process for the low-density TiN coating, a study has been made jointly with Mitsubishi Materials Corporation. By using a mixture of $TiCl_4$, NH_3 and H_2 , the TiN coating whose density is as low as 40%T.D. has been formed on static graphite substrates.

3. Properties of TRU nitrides

3.1 Thermal conductivity of NpN

Thermal conductivity is one of the most important properties for fuel design. Especially the information on Np is essential because of its large production and long half life time compared with other minor actinides. The thermal conductivity of NpN was determined from the thermal diffusivity measured by a laser-flash method[14].

Thermal diffusivity of NpN was measured from 740 K to 1,600 K in a vacuum on both heating and cooling runs. Details of the apparatus used were described elsewhere[15]. Thermal conductivity is given as a product of thermal diffusivity, bulk density and specific heat capacity. Unfortunately the last one of NpN is not available. Therefore, in this study the specific heat capacity, C_p is derived from the empirical equations presented by Kelley[16] and Kubaschewski[17] as follows;

$$C_p(\text{J/mol K}) = 52.85 + 2.55 \times 10^{-3}T - 8.37 \times 10^{-5}T^2.$$

Thermal conductivity of NpN is shown in fig. 2, together with those of UN and PuN[18]. The correction of porosity was made by use of the Maxwell-Eucken equation. The thermal conductivity of NpN gradually increases with temperature in a similar way to UN and PuN. The thermal conductivity of actinide mononitrides shows a tendency to decrease with the atomic number of actinides and also that the conductivity of NpN lies between those of UN and PuN.

3.2 Vaporization behavior of NpN and AmN

Vaporization behavior of actinide nitrides affects the migration of actinides during the fabrication process and the performance of failed fuel pins. From these viewpoints, the partial pressure of Np over NpN was determined by mass spectrometry with a Knudsen effusion cell.

Several mg of NpN synthesized by carbothermic reduction was used for mass spectrometry. The experimental procedure is similar to the determination of Pu pressure over PuN and (U,Pu)N described in an earlier paper[19]. The observed partial pressure of Np over NpN is shown in fig. 3, which indicates the change of the slope of the partial pressure plotted against the reciprocal of absolute temperature around 1,950 K. The phenomena was observed only at the first heating. On the following cooling and repeated runs, Np pressure was found to

be close to that over neptunium metal[20]. Therefore, it is suggested from these results that NpN evaporates congruently below 1,950 K, but at higher temperature it forms a liquid metal phase as UN does[21]. From mass spectrometric studies, PuN is reported to evaporate congruently[19,22], while UN forms a liquid phase and the partial U pressure over UN is similar to that over U metal. It could be said from the present study that NpN shows an intermediate behavior between UN and PuN.

Vaporization of Am can be a problem in the fabrication of the Am-containing fuels regardless of their chemical forms. Evaporation of americium from the nitride was also analyzed using the vaporization data on PuN containing Am[19]. The PuN sample contained about one percent Am-241 of the total heavy metal. By the analysis of the vaporization behavior, it was estimated that the second-law enthalpy of formation of AmN is -294kJ/mol at 1,600 K, which is close to those of UN and PuN.

4. Electrorefining of TRU nitrides

A pyro-chemical process has been developed for the metallic fuel cycle represented by the IFR program[23]. The introduction of the pyro-chemical process will lead to the design of a compact reprocessing facility combined with a fuel fabrication process. Recently it was indicated from thermodynamic considerations that nitride fuel might be also able to be treated by a pyro-chemical process, where actinide nitrides dissolve into fused salt as metal ions at an anode, while actinide metals are deposited at a cathode[24].

Uranium mononitride was treated by electrorefining with LiCl-KCl eutectic salt. Uranium mononitride powder was charged in a graphite anode basket. The cathode was a thin molybdenum rod. As an oxidizer, CdCl₂ was initially added to LiCl-KCl. Electrolysis was made at 450°C. It was confirmed that UN was completely dissolved and uranium metal was deposited on the cathode. Recently Russian researchers also reported the recovery of 500 g uranium metal from UN by a pyro-chemical process[25]. These results confirm the validity of the nitride fuel cycle combined with fused salt electrorefining.

For fast reactors, a nitride fuel cycle combined with a pyro-chemical process with fused salt electrorefining and refabrication has been proposed[2]. The same concept might be available for the nitride fuel cycle for TRU burning. At present, an electrorefiner and gloveboxes with an atmosphere of high purity argon gas are being installed in order to apply the method of fused salt electrorefining to the nitrides of Np and Pu. The preliminary experiments are planned to start in spring, 1995.

5. Summary

The recent research and development of nitride fuel and its fuel cycle for the transmutation of minor actinide are described. The fuel fabrication method investigated in JAERI is as follows:

- (1) Direct conversion of actinide nitrate salt from reprocessing process to fuel particles
- (2) Preparation of minor actinide nitride by carbothermic reduction
- (3) Coating of TiN to fuel particles by the CVD method.

The basic fuel properties of mononitride of minor actinides were determined using the samples synthesized carbothermic reduction. It is shown that the thermal conductivity of NpN lies between those of UN and PuN. With regard to the vaporization behavior of NpN, it is suggested that NpN evaporates congruently below about 1,950 K, while it forms a liquid phase at higher temperature. The vapor pressure of Am over AmN is also estimated using the data on the Am-containing mononitride of reactor-grade plutonium. Finally, the studies on an innovative nitride fuel cycle combined with fused salt electrorefining and refabrication of particle fuel are introduced.

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Table 1 Composition of NpN synthesized by carbothermic reduction

nitrogen	carbon	Oxygen
5.70 wt%	0.09 wt%	0.03 wt%

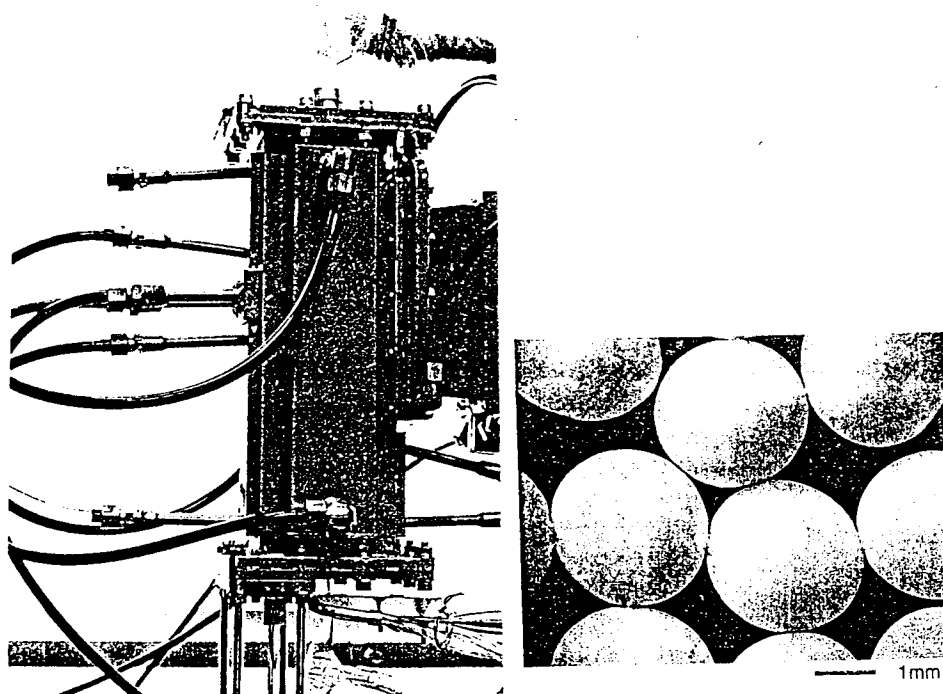


Fig. 1 A 2.45GHz microwave gelation apparatus and microspheres of ammonium uranates

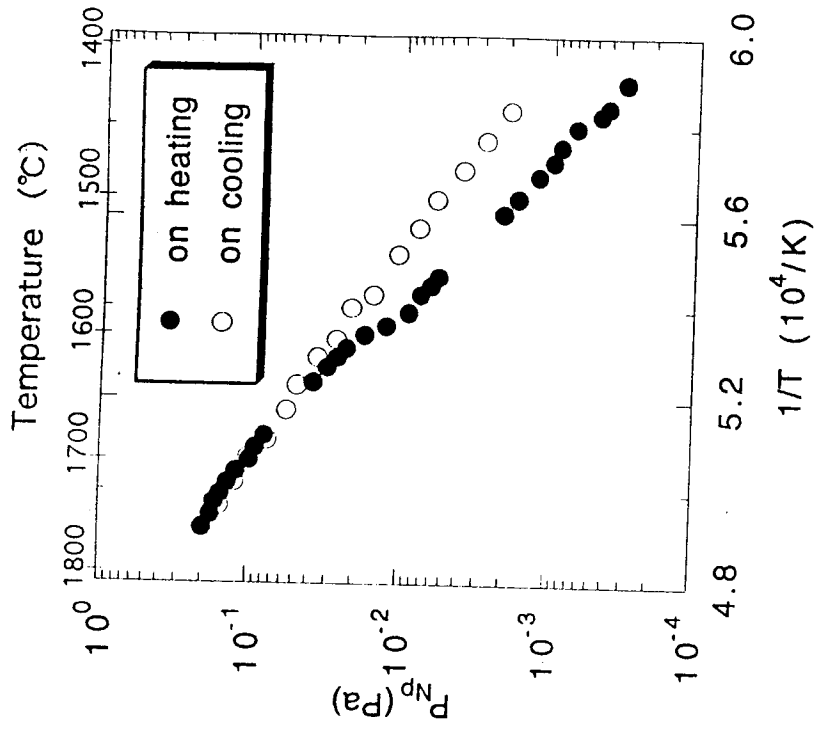


Fig. 3 Vapor pressure of Np over NpN

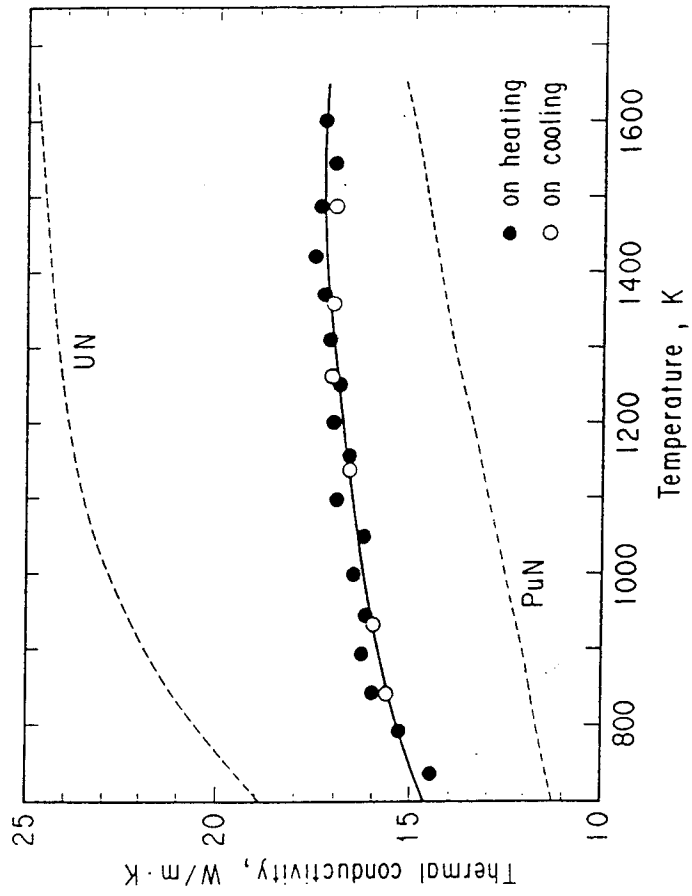


Fig. 2 Thermal conductivity of NpN