



4. Session B-2: Property Measurements

4.1 Properties of Minor Actinide Nitrides

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Abstract

The present status of the research on properties of minor actinide nitrides for the development of an advanced nuclear fuel cycle based on nitride fuel and pyrochemical reprocessing is described. Some thermal stabilities of Am-based nitrides such as AmN and (Am,Zr)N were mainly investigated. Stabilization effect of ZrN was clearly confirmed for the vaporization and hydrolytic behaviors. New experimental equipments for measuring thermal properties of minor actinide nitrides were also introduced.

1. Introduction

Nitrides fuel has been widely studied as one of advanced fuels of fast reactors, because actinide nitrides have many advantages compared with the oxides, such as higher heavy-metal density, good thermal properties, miscibility among the actinide nitrides, and so on. Recently, large R & D efforts devoted to transmutation of long-lived radioactive elements including minor actinides (MA) are being done in Japan in the frame of the OMEGA program, for the management of high level, long-lived radioactive waste. The Japan Atomic Energy Research Institute (JAERI) has proposed the concept for transmutation of MA elements using accelerator-driven systems (ADS) [1], where MA nitride is adopted as a fuel material of the sub-critical core.

The research and development of nitrides fuel as an advanced fuel of fast reactors at JAERI included fabrication technologies, property measurements, irradiation tests and electrorefining. In this frame work, some thermal properties such as vaporization, heat capacity, thermal conductivity and thermal expansion were measured in UN, PuN, NpN and their solid solutions of (U,Pu)N, (U,Np)N and (Np,Pu)N.

Significant experience exists for U-based or Pu-based nitrides, but there is a lack of knowledge about the characteristics for MA-based nitrides as U-free fuels for ADS. The main disadvantage related to the use of MA-based nitrides fuel is relatively lower thermal stability, in particular, high-temperature stability in terms of vaporization in fabrication processes and reactor accidents. The addition of an inert matrix to improve the thermal properties of MA-based nitrides fuel has been suggested. ZrN is thought to be one of candidate materials for Am-based nitrides.

In the study the properties of UN, PuN, NpN and their solid solutions are overviewed, and the present status on property measurements of MA-based nitrides is summarized.

2. Properties of U, Np and Pu nitrides

Vaporization behavior of U-, Np-, Pu-based nitrides was investigated by a Knudsen-effusion mass-spectrometry [2-4]. UN vaporizes incongruently precipitating liquid uranium while PuN vaporizes congruently. For NpN, the vapor pressure of Np(g) was similar to that of Np(g) over liquid Np metal. The vapor pressures of UN, NpN, and PuN increase in this order at an identical temperature.

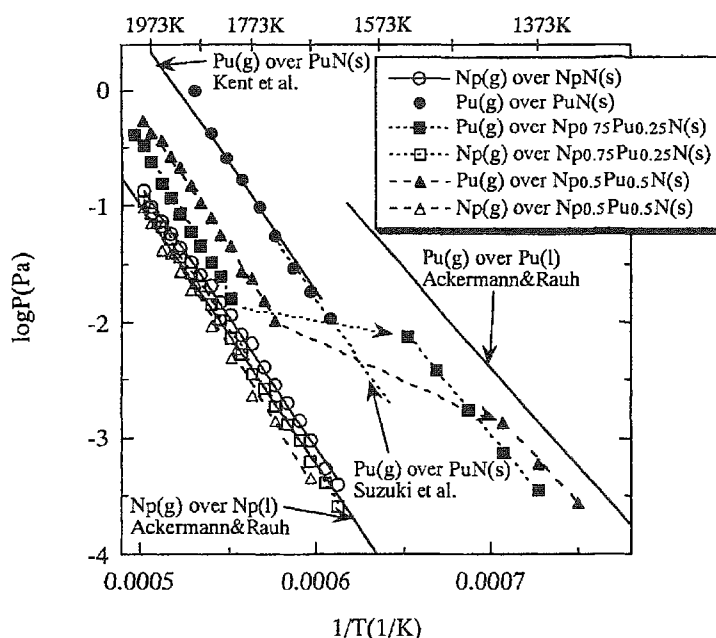


Fig.1 Vaporization behavior of (Np,Pu)N solid solutions

For (U,Pu)N, the partial pressures of U(g) and Pu(g) depended on the composition of the solid solutions. (U,Pu)N vaporized congruently and no liquid phase formed under the experimental conditions. For (Np,Pu)N as shown in Fig.1, the vapor pressures of Np(g) over solid solutions of (Np,Pu)N showed a similar temperature dependence to that over Np(l), which suggested the precipitation of liquid neptunium during the measurements. On the other hand, rather complicated temperature dependence

was found for Pu(g) over the solid solutions (Np,Pu)N. At temperatures higher than 1773 K the vapor pressures of Pu(g) reflected those over (Np,Pu)N being influenced by the Pu/(Np+Pu) ratio in solid phase, while at temperatures lower than 1473 K the vapor pressures of Pu(g) observed were those over liquid plutonium that may have been precipitated during the measurements..

The specific heat capacities of UN, NpN, and PuN were measured with a differential scanning calorimeter (DSC) in the temperature range from 323 to 1023 K [5]. The heat capacities of UN and PuN measured in this study agreed with the data in the literature within experimental errors. The heat capacity of NpN was found to be nearly the same as those of UN and PuN.

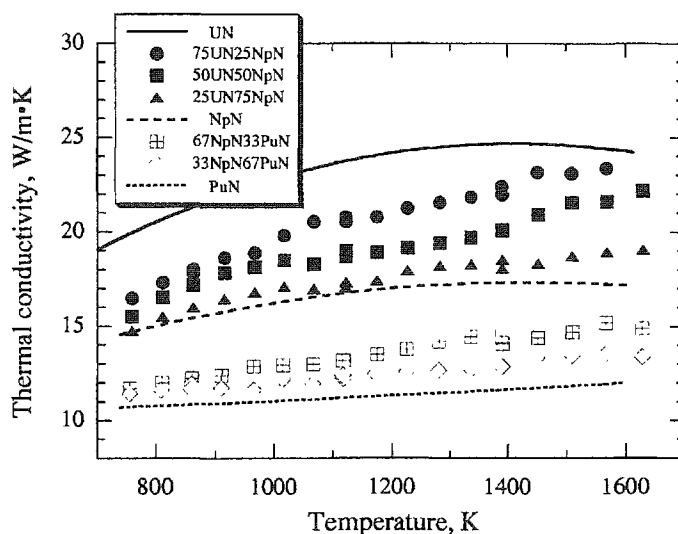


Fig.2 Thermal conductivity of (U,Np)N and (Np,Pu)N solid solutions

The thermal diffusivities of UN, NpN, PuN and the solid solutions of (U, Pu)N, (U, Np)N, and (Np, Pu)N were measured by the laser-flash method from 740 to 1630 K and the thermal conductivities were determined as a function of temperature, as shown in Fig.2 [6-8]. The thermal conductivities of the actinide nitrides gradually increase with temperature over the temperature range investigated. For these nitrides, the electronic component contributes dominantly to the total thermal conductivity, and the increase in the thermal conductivity is due to the increase in the electronic component. It is also found that the thermal conductivity decreases with increasing atomic number from UN to PuN. It is probable that the decrease is caused by the decrease in the electronic component to the thermal conductivity.

3. Properties of minor actinide nitrides

3.1 Hydrolytic behavior

Hydrolytic behavior 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.3 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 increase in carbon content from 0.3 to 2 wt% suggests that a part of Am(OH)₃ reacted with CO₂ in the atmosphere to form a hydrooxy-carbonate, AmOHCO₃ and/or a carbonate, Am₂(CO₃)₃.

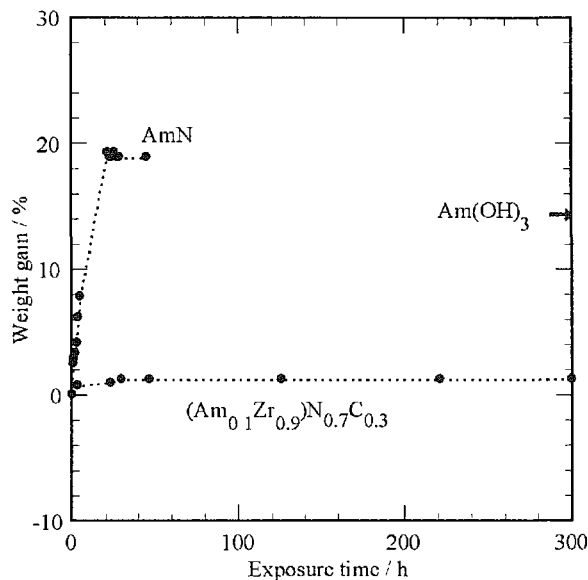


Fig.3 Weight gains of AmN and (Am,Zr)N in air.

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.

3.2 Vaporization behavior

Vaporization behavior of AmN and (Am,Zr)N solid solution in He gas flow was investigated by measuring N₂ 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.

Fig.4 shows the vaporization behavior of AmN and (Am,Zr)N as a function of temperature, where the 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 vaporization of Am on the nitride.

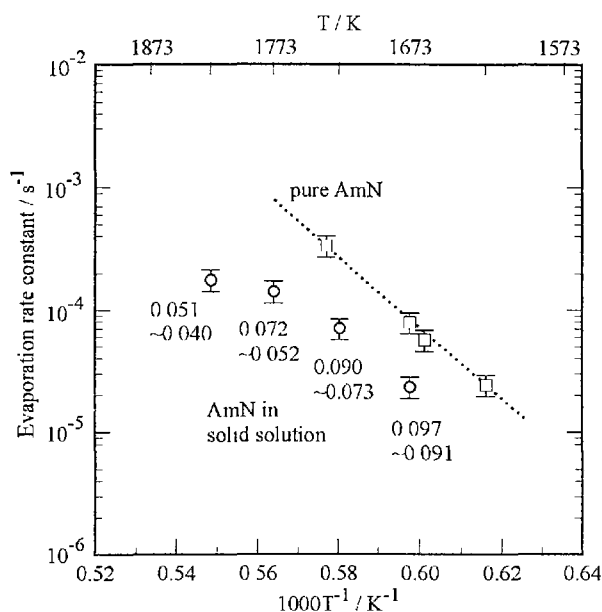


Fig. 4 Arrhenius plots of the evaporation rate constants for AmN and $(\text{Am}_{0.1}\text{Zr}_{0.9})\text{N}_{0.85}\text{C}_{0.15}$.

On the other hand, the equilibrium vapor pressure of Am over AmN was estimated with the Gibbs free energy minimizer ChemSage. It was found that the vapor pressure of Am strongly depends on the partial pressure of N_2 in atmosphere and that high partial pressure of N_2 is very effective to depress the vaporization and loss of Am at high temperature.

4. Installation of experimental equipments

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 WASTE in the Tokai Research Establishment of JAERI. The thermal diffusivity measuring equipment based on laser flash method was specially designed to make measuring very small samples of MA nitrides and handling the samples in an inert atmosphere possible. Fig.5 shows the equipment before installation and the

Ar-atmosphered inert glove box, in which oxygen and moisture contents are controlled to be below a few ppm.

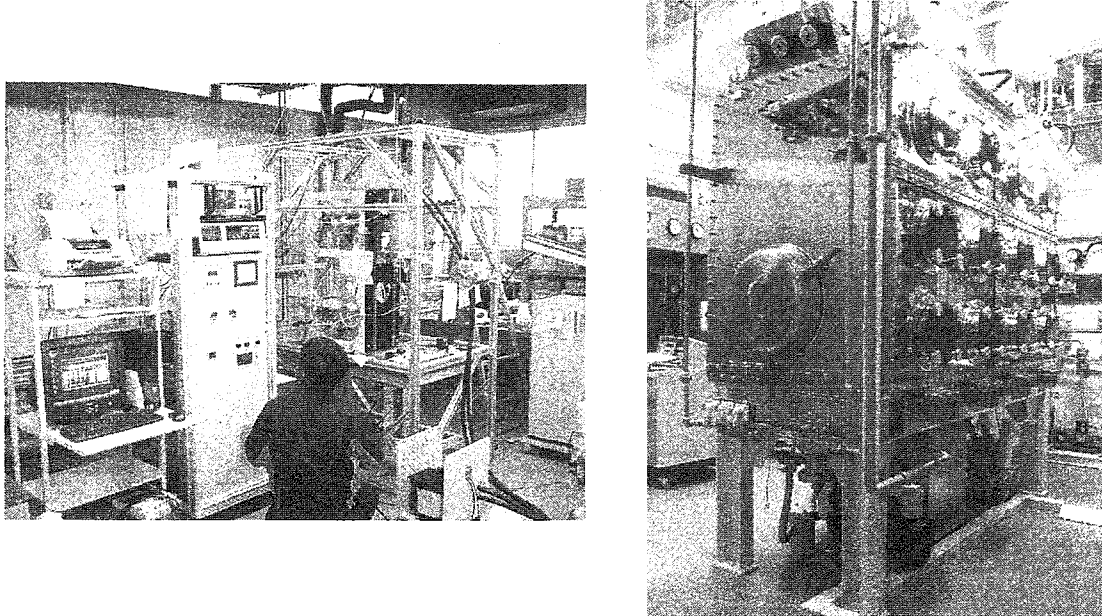


Fig.5 The thermal diffusivity measurement equipment and the inert glove box.

The specific heat capacity measuring equipment based on drop calorimetry method was also installed in an air-atmosphered glove box. It allows to measure the heat capacity of very small samples ($<100\text{mg}$). Fig.6 shows the equipment before installation and the glove box.

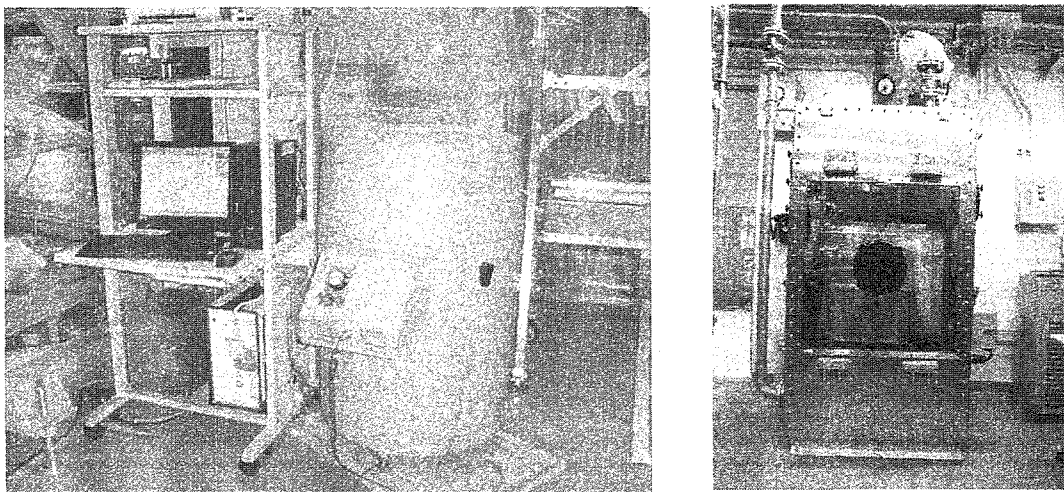


Fig.6 The specific heat capacity measuring equipment and the glove box

Acknowledgements

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