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Dissolution and chemical analysis of Zr-based lanthanide nitrides

Hirokazu Hayashi[a*] and Rikiya Chiba[a,b]

[a]Japan Atomic Energy Agency, 2-4 Shirakata, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan; [b]Present affiliation: Nuclear Engineering Co. Ltd., 3129-29 Muramatsu, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1112, Japan

Dissolution behavior of Zr-based lanthanide nitride solid solutions, which are surrogates of Zr-based transuranium nitrides, in nitric acid was examined. Powder sample of the matrix material, ZrN was completely dissolved with 7.4 mol/L HNO_3 at 383 K in 20 hours or 7.7 mol/L HNO_3 at room temperature in 134 days. LnN-ZrN solid solutions were completely dissolved with milder conditions; 0.25GdN-0.75ZrN was with 7.5 mol/L HNO_3 in 6 days, and 0.40DyN-0.60ZrN was with 7.7 mol/L HNO_3 in 1 day or 1.0 mol/L in 20 days at room temperature. These results suggest that it became easier to dissolve LnN-ZrN solid solution with increasing the contents of LnN. From chemical analysis of LnN-ZrN samples, a change of the metal compositions during pellet sample fabrication process was observed for 0.40DyN-0.60ZrN, though not for 0.25GdN-0.75ZrN. The change of the metal composition in 0.40DyN-0.60ZrN sample is considered to be due to vaporization of Dy during the heating process.

Keywords: minor actinide; transuranium elements (TRU); nitride fuel; uranium-free; inert matrix; nitric acid; lanthanide nitride; zirconium nitride; transmutation fuel

1. Introduction

Uranium-free nitride fuel has been chosen as the first candidate for transmutation of long-lived minor actinides (MA: Np, Am, Cm) using sub-critical accelerator-driven system (ADS) under the double strata fuel cycle concept by Japan Atomic Energy Agency (JAEA). The advantages of nitride fuel are good thermal properties and large mutual solubility among actinide elements. Typical composition of the fuel is considered as 30 wt.% of MA nitride, 20 wt.% of Pu nitride, and 50 wt.% of ZrN (corresponds to $MA_{0.18}Pu_{0.12}Zr_{0.70}N$). Pu is added to mitigate the burn-up reactivity swing, and ZrN is the first candidate of the dilution material to adjust the power density. Flexibility of the ratio of MA, Pu, and Zr in the solid solution type fuel compound (MA,Pu,Zr)N is appropriate for the detailed design of the fuel [1-3].

In the fuel fabrication process, analysis of the samples is important because the composition of the nuclides should be controlled precisely. In addition, recovery and reuse of the transuranium elements (TRU) contained in the scraps generated during the process is necessary to reduce the losses of TRU [2,3]. Both of them need dissolution of Zr-based nitrides into aqueous solution. On the other hand, direct dissolution of spent nitride fuels into nitric acid is one of the key technologies on adapting aqueous reprocessing to spent Zr-based nitride fuels.

Actinide nitrides and U-based nitride fuel have been reported to be easily dissolved in nitric acid [4,5]. But, chemical stabilization of actinide nitrides in Zr-based nitride is thought to affect the dissolution behavior, which has not been studied enough [6-8].

In this study, dissolution behavior of Zr-based lanthanide nitride (LnN) solid solutions, which are surrogates of Zr-based TRU nitrides, in nitric acid was examined. Chemical analysis of the LnN-ZrN dissolved in nitric acid was also carried out to investigate composition change in pellet fabrication process.

2. Experimental

2.1. Sample preparation

ZrN, GdN, and DyN samples were prepared by nitridation of the hydrides in N_2 gas flow; the hydrides had been prepared from the corresponding metal rods. Solid solution samples of 0.25GdN-0.75ZrN and 0.40DyN-0.60ZrN were prepared by heating the compacted mixtures of well ground nitrides at 1973 K and 1873 K, respectively, for 5 hours under N_2 gas flow as in [9]. High density pellet samples of 0.25GdN-0.75ZrN (90%TD) and 0.40DyN-0.60ZrN (75%TD) were prepared by sintering the green pellets at 1973 K and 1923 K, respectively, for 5 hours under N_2 gas flow. Powder samples used in the experiments were obtained by grinding the pellet samples with a tungsten carbide mortar. The obtained particle sizes were found to be smaller than 150 μm in case of ZrN samples.

X-ray diffraction (XRD) and quantitative analyses of

*Corresponding author. Email: hayashi.hirokazu55@jaea.go.jp

nitrogen, oxygen and carbon were carried out to identify the products as in the previous paper [10].

2.2. Dissolution and analyses

Powder samples of nitrides (20 ~ 70 mg) were dissolved in nitric acid solution or water (20 ~ 40 mL) at room temperature or ~383 K. The sample in a conical flask with a condenser was heated with a hotplate. The sample for dissolution experiments was stirred with a magnetic stirrer coated with polytetrafluoroethylene. Concentrations of metal elements (Zr, Gd, Dy) were determined with ICP-AES using sampled solutions.

Chemical compositions of the samples were determined from the concentrations of metal elements measured with the solutions in which the entire powder samples were dissolved, with the results of quantitative analyses of light elements (nitrogen, oxygen, and carbon).

3. Results and discussion

3.1. Samples

Table 1 shows the lattice parameters determined with XRD and the composition of light elements in nitride samples. Analytical results indicate that homogeneous solid solutions were formed and the purity of the samples are high enough for the following experiments.

Table 1. Lattice parameters and the compositions of light elements in nitride samples.

Sample	Lattice Parameter (nm)	Carbon (wt%)	Nitrogen (wt%)	Oxygen (wt%)
ZrN*	---	ND	12.82 ± 0.14	<0.036
ZrN	0.4575	ND	12.94 ± 0.14	<0.054
GdN	0.4978	ND	7.57 ± 0.05	0.456 ± 0.018
DyN	0.4900	ND	7.68 ± 0.07	0.291 ± 0.014
0.25GdN -0.75ZrN	0.4662	ND	11.28 ± 0.08	0.322 ± 0.009
0.40DyN -0.60ZrN	0.4688	0.058 ± 0.001	10.16 ± 0.06	0.402 ± 0.011

ND: not determined, * This sample was used only in dissolution test of ZrN at 383 K.

3.2. Dissolution behavior

Figure 1 shows dissolution behavior of 40.95 mg of ZrN powder in 7.4 mol/L HNO_3 (40 mL) at 383 K. No residue was found after heating 30 hours. Data of preliminary experiment obtained with using 19.6 mg of ZrN powder in 7.7 mol/L HNO_3 (20 mL) at 383 K are also shown in Figure 1. **Table 2** shows our result comparing with the reported ones. Our result shows that ZrN sample can be entirely dissolved with boiling 7.4 mol/L HNO_3 in 20 hours.

Figures 2 and **3** show dissolution behavior of powder samples of ZrN, 0.25GdN-0.75ZrN, and 0.40DyN-0.60ZrN in ~7.5 mol/L HNO_3 (20 mL) at room temperature. Detailed conditions of the experiments are shown in **Table 3**. The results show that complete

dissolution of ZrN needed 134 days at room temperature. On the other hand, the solid solution samples were dissolved in a shorter period. Complete dissolution of 0.25GdN-0.75ZrN and 0.40DyN-0.60ZrN needed 6 days and less than 1 day, respectively. These results suggest that with increasing the contents of LnN, it becomes easier to dissolve the solid solution of LnN-ZrN. This tendency is consistent with the previous report, in which $U_{0.2}Zr_{0.8}N$ disk sample is easier to be dissolved than ZrN sample as shown in Table 2 [6].
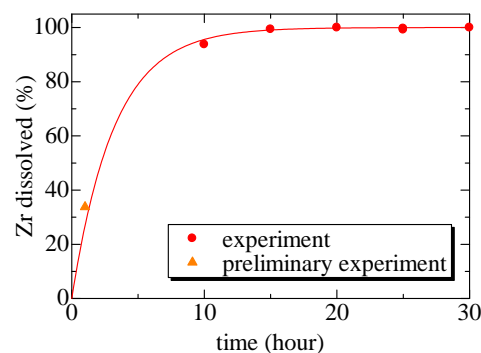

Figure 1.   Dissolution behavior of powder ZrN sample in 7.4 mol/L HNO_3 at 383 K.
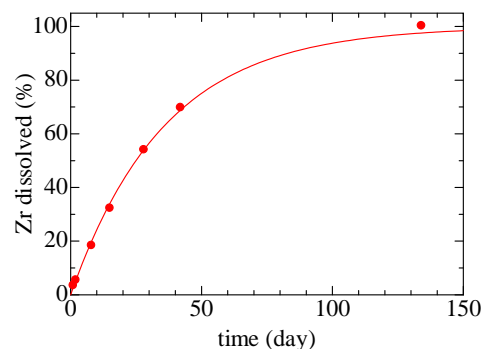

Figure 2.   Dissolution behavior of powder ZrN sample in 7.7 mol/L HNO_3 at room temperature.

Table 2.   Experimental results on dissolution behavior of ZrN and Zr-based nitride with boiling nitric acid.

Sample form	mg	HNO_3 mol/L, mL	Results	Ref.
ZrN powder	40.95	7.4, 40	100% in 20h	This work
ZrN powder	-	10, 50	95% in 10h	6
ZrN disk	300 ~600	7, 50~100	1.5% in 34h	7
$U_{0.2}Zr_{0.8}N$ disk	-	10, 50	85% in 6h	6

Table 3.   Experimental conditions of dissolution behavior in ~7.5 mol/L HNO_3 (20 mL) at room temperature.

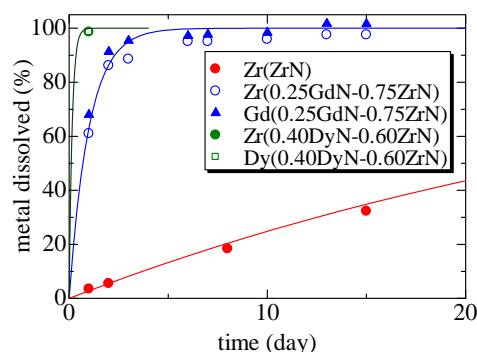| Sample	Sample weight (mg)	Conc. of HNO_3 (mol/L)
ZrN	21.88	7.7
0.25GdN-0.75ZrN	21.65	7.5
0.40DyN-0.60ZrN	19.97	7.7

Figure 3.　Dissolution behavior of powder nitride samples in ~7.5 mol/L HNO_3 at room temperature.

Dissolution behavior of powder 0.40DyN-0.60ZrN sample (19.88 mg) in 1.0 mol/L HNO_3 (20 mL) at room temperature is shown in **Figure 4**. Complete dissolution was achieved in 20 days, which is longer than the period with 7.7 mol/L HNO_3. On the other hand, after heating 19.99 mg of 0.40DyN-0.60ZrN powder sample in water (20 mL) at 373 K for 10 hours, less than 0.2 % of the metal elements were dissolved in the solution. The residue after drying at 373 K was identified as the mixture of the nitride and Dy_2O_3 by XRD. The results show that the LnN-ZrN sample can be dissolved in dilute nitric acid but not in water.
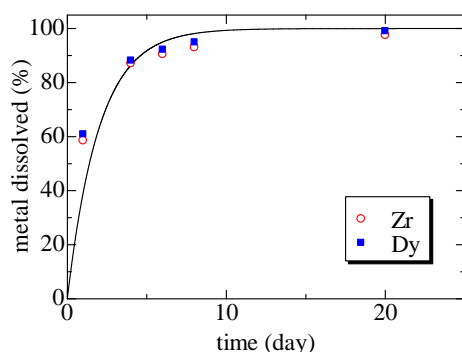

Figure 4.　Dissolution behavior of powder 0.40DyN-0.60ZrN sample in 1.0 mol/L HNO_3 at room temperature.

3.3. Chemical analyses

Condition of complete dissolution of 0.25GdN-0.75ZrN and 0.40DyN-0.60ZrN samples was set according to the dissolution behavior of the samples in ~7.5 M HNO_3. The samples were heated to 383 K in 0.5 hour, kept at 383 K for an hour, and cooled down overnight.

Tables 4 and **5** show the atomic ratios of 0.25GdN-0.75ZrN and 0.40DyN-0.60ZrN determined from the analyses, respectively. Three measurements on the same sample show similar values. The total weight ratios which were identified by the quantitative analyses were more than 99.5 % of the sample weight as in **Table 6**. Therefore more than 99.5 % of the samples were considered to be dissolved in the solutions.

The compositions of the solid solution samples were determined to $Gd_{0.249}Zr_{0.751}N_{0.983}O_{0.025}$ and $Dy_{0.389}Zr_{0.611}N_{0.971}O_{0.034}C_{0.007}$, respectively. Obtained

Gd/Zr ratio is close to that derived from the weight ratio of GdN and ZrN used in sample preparation. But, Dy/Zr ratio becomes lower than that derived with a similar manner.

Table 4.　Atomic ratios of 0.25GdN-0.75ZrN sample. The ratio of Zr+Gd is defined as unity.

Element	No.1	No.2	No.3	Ave.
	38.04 mg	66.80 mg	39.77 mg	
N	0.981	0.983	0.986	0.983
O	0.024	0.025	0.025	0.025
Zr	0.749	0.751	0.752	0.751
Gd	0.251	0.249	0.248	0.249

Table 5.　Atomic ratios of 0.40DyN-0.60ZrN sample. The ratio of Zr+Dy is defined as unity.

Element	No.1	No.2	No.3	Ave.
	42.25 mg	54.66mg	41.88mg	
C	0.007	0.007	0.006	0.007
N	0.973	0.972	0.970	0.971
O	0.034	0.034	0.034	0.034
Zr	0.613	0.610	0.610	0.611
Dy	0.387	0.390	0.390	0.389

Table 6.　Percentages of the elemental weight which were identified by the quantitative analyses.

Element	0.25GdN-0.75ZrN	0.40DyN-0.60ZrN
C	ND	0.058±0.001
N	11.28±0.08	10.16±0.06
O	0.322±0.009	0.402±0.011
Zr	56.1±0.1	41.6±0.1
Gd	32.1±0.2	---
Dy	---	47.3±0.2
Total	99.8±0.2	99.5±0.2

ND: not determined.

Changes of the metal compositions in nitride samples having Am by heating in N_2 (or $N_2/\sim4\%$ H_2) atmosphere, which is more preferable to suppress vaporization of AmN than other atmosphere, have been reported [11-13]. Sintering of PuN having 1.5% of decay product Am-241 in N_2 at 2073 K and that of $Am_{0.1}Zr_{0.9}N_{0.85}C_{0.15}$ in N_2/H_2 atmosphere at 1773 K indicated the weight losses (11% and 3.6%). The losses are considered to be due to vaporization of Am [11, 12], because vapor pressure of Am over AmN is much higher than that of Pu over PuN [14]. In Figure 5, the vapor pressure data are shown with those of LnN and ZrN. Among lanthanides, Dy metal shows large vapor pressure [15]. Though vapor pressure data of Dy over DyN (p(Dy over DyN)) have not been reported, they can be derived using other thermochemical data according to Eq. (1) with supposing congruent vaporization,

$$\ln(p(Dy \; overDyN)) = \frac{2}{3}\left(\frac{\Delta G(DyN) - \Delta G(Dy(g))}{RT} + \ln(2(\frac{m_{Dy}}{m_{N2}})^{1/2})\right), \quad (1)$$

where $\Delta G(DyN)$ and $\Delta G(Dy(g))$ are the Gibbs free energies of formation of DyN and gaseous Dy, m_{Dy} and

m_{N2} are molecular weights of Dy and N_2, respectively. Assuming $\Delta G(DyN)$, which have not been reported, equals to the values of $\Delta G(AmN)$ [14], p(Dy over DyN) can be expressed with Eq. (2).

$$\log(p(Dy \quad overDyN)/Pa) = -\frac{19188}{T} + 11.829 \quad (2)$$

Vapor pressure of Zr over ZrN is estimated with a similar manner using thermochemical data [16] as

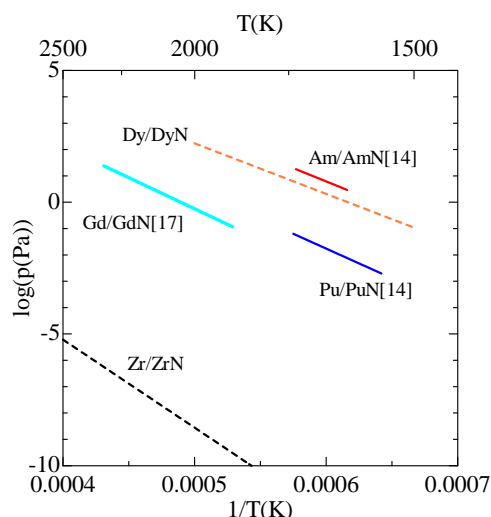$$\log(p(Zr \quad overZrN)/Pa) = -\frac{33475}{T} + 8.189. \quad (3)$$

Figure 5. Equilibrium vapor pressure of selected nitrides.

Figure 5 indicates that the estimated vapor pressure of DyN is higher than those of GdN [17] and ZrN, and as high as those of AmN. Decrease of Dy component in 0.40DyN-0.60ZrN sample is considered to be due to vaporization of DyN component during heating process, as reported for the nitrides containing AmN.

4. Conclusion

Complete dissolution of ZrN powder in ~7.5 M nitric acid solution needed 20 hours at 383K, or 134 days at room temperature. Dissolution of Zr-based lanthanide nitrides (0.4DyN-0.6ZrN and 0.25GdN-0.75 ZrN) were completed with milder conditions. With increasing LnN contents, dissolution of Zr-based nitride becomes easier to achieve. By determining the chemical compositions of the Zr-based lanthanide nitride, vaporization of Dy (surrogate of Am) during the pellet fabrication process was certified.

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