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Heat capacities of NpN and AmN

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ABSTRACT

The heat capacities of NpN and AmN were determined with the drop calorimetry method. The NpN and AmN samples were prepared by the carbothermic reduction of the respective dioxides. The heat capacity of NpN obtained was in good agreement with the reported values in the temperature range from 334 to 1067 K, which was close to those of UN and PuN. The heat capacity of AmN was obtained experimentally for the first time, which was slightly smaller than those of UN, NpN and PuN in the temperature range from 354 to 1071 K.

1. Introduction

The long-term hazard of radioactive wastes arising from nuclear energy production is a matter of discussion and public concern. To reduce the radiotoxicity of the high-level waste and use the repository efficiently, the partitioning and transmutation of minor actinides (MAs: Np, Am, Cm) as well as plutonium is an option for the future nuclear fuel cycle. Many concepts have been proposed on the fuels together with advanced reactors or accelerator driven systems (ADS). Among various fuel types, nitride fuel is one of the candidates for the MA-bearing fuels because of the high melting points, good thermal conductivities, and mutual solubility.

Heat capacities of MA nitrides are among fundamental thermophysical properties for the design of MA-bearing fuels and analysis of irradiation behavior, especially at a transient condition [1–4]. Some results have been reported for the heat capacities of UN [5,6], while those of NpN [7] and PuN [8] are scarce. Especially, no experimental data for that of AmN are available in literature. In this study, the enthalpy increments of NpN and AmN were measured by use of the drop calorimeter in a glove box, and then the heat capacities of NpN and AmN were determined.

2. Experimental

2.1. Samples

The NpN and AmN samples were prepared by the carbothermic reduction of the respective dioxides $^{237}NpO_2$ and $^{243}AmO_2$: characteristics of the $^{237}NpO_2$ and $^{243}AmO_2$ powders provided from the State Scientific Center of Russia were described elsewhere [9,10]. Each powder was mixed with carbon powder at C/M (M: metal) ratios of 2.84 and 2.80, respectively. The mixtures were compacted and heated at 1683 and 1693 K in flowing N_2 gas at 500 ml/min, respectively. After the CO gas release measured by use of an infrared spectrometer subsided, the flowing gas was replaced by $N_2 + 4\% H_2$ mixed gas to remove the residual carbon. The additional heating was continued at 1793 K until the CO gas release subsided again. The products of carbothermic reduction were ground and pressed to disks. The NpN and AmN disks were sintered at 2023 K and 1893 K in flowing $N_2 + 4\% H_2$ gas, respectively. Characteristics of NpN and AmN samples for the enthalpy increment measurements are summarized in Table 1. The oxygen and nitrogen contents were measured with an apparatus (HORIBA, EMGA-550) based on the inert gas fusion technique. The carbon content was measured with an apparatus (CE Instruments, NC-2500) based on the combustion technique. The samples were subjected to powder X-ray diffraction analysis with Cu Kα radiation to determine the lattice parameters and to identify the phases.

2.2. Procedures

The enthalpy increments were measured by using a twin-type drop calorimeter (SETARAM, HT-1000) in the glove box. The apparatus consisted of two differential calorimetric units located in two cylindrical wells. The temperature difference between two calorimetric units was detected by Pt–Pt10%Rh thermocouples.

The samples were loaded in platinum containers. The container was evacuated and sealed in argon gas atmosphere in the background pressure of about 10 kPa. The sapphire was also sealed in

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Table 1
Characteristics of NpN and AmN samples for the enthalpy increment measurements

	NpN	AmN
Weight (mg)	102.06	42.09
Pt container weight (mg)	521.58	373.93
Nitrogen (wt%)	5.48 ± 0.10	4.96 ± 0.10
Oxygen (wt%)	0.32 ± 0.15	1.22 ± 0.15
Carbon (wt%)	$\leqslant$0.05	0.21 ± 0.02
Lattice parameter (nm)	0.4895	0.4998

another container as the standard sample. The enthalpy increment of 'blank' Pt container without any sample was also measured.

The sample enclosed with the container was kept at room temperature for at least one hour in a polyethylene container placed above the calorimeter to assure the thermal equilibrium. The room temperature, which was measured with the thermometer placed in the polyethylene container, was within a range from 297 to 305 K. Then the sample was dropped into the calorimeter kept at a constant temperature. The heat flows of the samples Q were calculated by subtracting those of the Pt containers from those of the samples enclosed with the Pt containers. The heat flow Q is determined as $Q = Aq$, where A is the correction coefficient of the calorimeter and q is the non-corrected heat flow. The correction coefficient was determined as the ratio between literature heat flow per weight of sapphire $Q - Q_{298.15}$ [11] and experimental one of this study in the temperature range from 312 to 1121 K. The $Q - Q_{298.15}$ value of sapphire and the correction coefficient of the calorimeter are shown in Fig. 1.

The enthalpy increments of samples were obtained by multiplying the heat flow of samples by respective formula weights. The enthalpy increment $H - H_{298.15}$ values at various temperatures were well fitted to quadratic polynomial expression in temperature T

$$H - H_{298.15} = aT^2 + bT + c. \quad (1)$$

Since the room temperature (RT) was not constant, each $H - H_{298.15}$ values were obtained by subtracting $H_{298.15} - H_{\mathrm{RT}}$ values from $H - H_{\mathrm{RT}}$ values. The heat capacity was obtained from the derivative of Eq. (1) with respect to temperature and is given by

$$\mathrm{Cp} = 2aT + b. \quad (2)$$

3. Results and discussion

Fig. 2 shows the enthalpy increments of NpN and AmN. No thermal anomalies were observed. The experimental data of NpN and AmN were fitted to quadratic polynomial equation using the least squares method. The result for NpN is

$$H - H_{298.15}\ (\mathrm{kJmol^{-1}}) = 9.358 \times 10^{-6}T^2 + 0.04275T - 13.63 \quad (3)$$

for the temperature range from 334 to 1067 K and the result for AmN is

$$H - H_{298.15}\ (\mathrm{kJmol^{-1}}) = 7.816 \times 10^{-6}T^2 + 0.04244T - 14.09 \quad (4)$$

for the temperature range from 354 to 1071 K. The uncertainties of the heat capacities for NpN and AmN ascribed to the statistical error of the enthalpy increments were ±3.2% and ±7.0%, respectively. The heat capacities of NpN and AmN were first derivative of Eqs. (3) and (4) with respect to temperature.

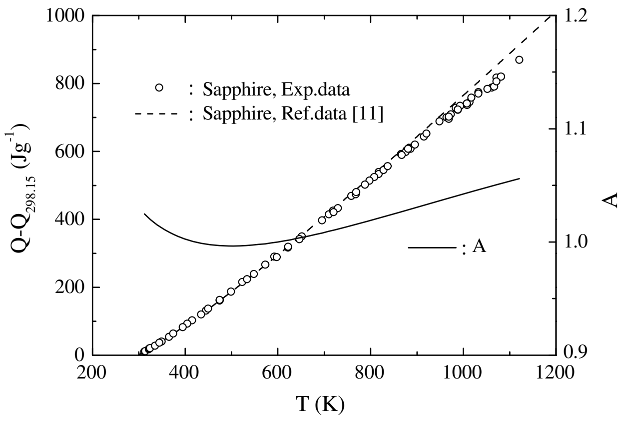

Fig. 1. Heat flow per weight of sapphire and the correction coefficient A of the calorimeter.

The heat capacity of NpN obtained is expressed by

$$\mathrm{Cp}\ (\mathrm{Jmol^{-1}K^{-1}}) = 1.872 \times 10^{-2}T + 42.75 \quad (5)$$

and shown in Fig. 3, together with the reported value for NpN [7] that was measured by the differential scanning calorimetry. It is seen in Fig. 3 that the heat capacity of NpN obtained was in good agreement with the reported value.

The heat capacity of AmN obtained is expressed by

$$\mathrm{Cp}\ (\mathrm{Jmol^{-1}K^{-1}}) = 1.563 \times 10^{-2}T + 42.44 \quad (6)$$

and shown in Fig. 4, together with those of UN [6], NpN and PuN [8]. The heat capacity of NpN was close to those of UN and PuN. On the other hand, that of AmN was slightly smaller than those of UN, NpN and PuN in the temperature range investigated. However, consider-

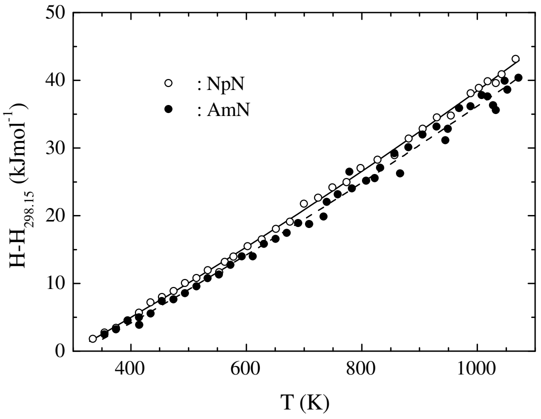

Fig. 2. Enthalpy increment $H - H_{298.15}$ values of NpN and AmN.

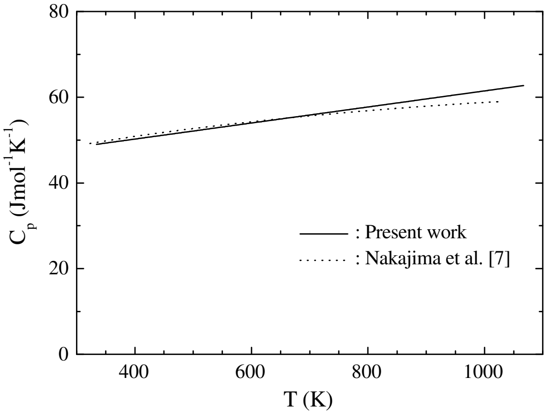

Fig. 3. Heat capacity of NpN together with reported values [7].

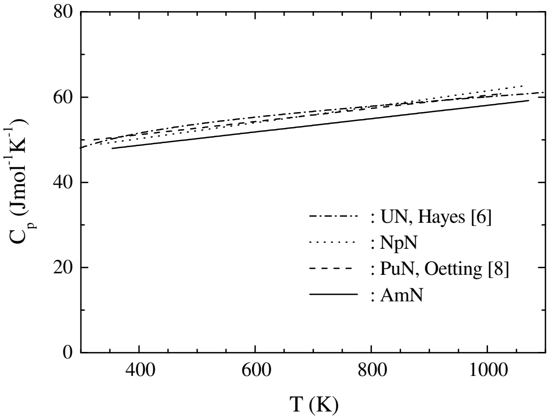

Fig. 4. Heat capacity of AmN together with those of UN [6], NpN and PuN [8].

ing the uncertainty of the heat capacity, it is seen that actinide nitrides have similar heat capacities with similar temperature dependence.

4. Conclusions

The heat capacities of NpN and AmN were measured by the drop calorimetry method in the temperature range from 334 to 1067 K and from 354 to 1071 K, respectively. The following was concluded:

(1) The heat capacity of NpN was expressed by Cp $(\mathrm{Jmol}^{-1}\mathrm{K}^{-1}) = 1.872 \times 10^{-2}T + 42.75 \quad (334 < T \quad (\mathrm{K}) < 1067)$. The heat capacity of NpN was in good agreement with the value reported by Nakajima et al.

(2) The heat capacity of AmN was expressed by Cp $(\mathrm{Jmol}^{-1}\mathrm{K}^{-1}) = 1.563 \times 10^{-2}T + 42.44 \quad (354 \leqslant T \quad (\mathrm{K}) \leqslant 1071)$. The heat capacity of NpN was close to those of UN and PuN, while that of AmN was slightly smaller than those of UN, NpN and PuN.

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