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Thermodynamic study on α-U_2N_{3+x} using N-rich starting material ($x \geq 0.6$)

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Abstract

Equilibrium measurements were performed to obtain the N_2 pressure–composition isotherms in the 400 to 900°C temperature range for the single-phase α-U_2N_{3+x} (1.63<1.76) region using N-rich α-U_2N_{3+x} (atomic ratio N/U>1.80) as the starting material. The partial molar free energy, enthalpy and entropy are calculated as a function of nitrogen content. © 1998 Elsevier Science S.A.

Keywords: α-U_2N_{3+x}; Partial molar enthalpy; Partial molar entropy; Partial molar free energy; Pressure–temperature–composition relationship

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1. Introduction

α-U_2N_3 is a nonstoichiometric compound exhibiting a wide range of composition and usually contains more nitrogen than indicated by its chemical formula, which is often designated α-U_2N_{3+x}. α-U_2N_{3+x} is prepared by the reaction of metallic uranium or UH_3 with N_2 gas at normal pressure. Although Rundle et al. [1] stated that the formation of UN_2 required high nitrogen pressure (126 atm), Didchenko and Gortsema [2] reported that UN_2 could easily be prepared by passing NH_3 over UH_3 while raising the temperature to 1000°C. Trezebiatowski and Troc prepared α-U_2N_{3+x} with N/U atom ratios from 1.5 to 1.86 using the following methods [3]. Nitrides with N/U atom ratios from 1.5 to 1.71 were prepared by treating uranium powder with N_2. However, uranium nitrides with higher nitrogen content up to $UN_{1.86}$ could be obtained solely by the action of ammonia on UH_3. According to Berthold and Delliehausen [4], the reaction of UN or α-U_2N_{3+x} (N/U<1.76) with N_2 or NH_3 at pressures up to 200 atm could lead to the formation of $UN_{1.83}$ (in the case of N_2) or $UN_{1.86}$ (in the case of NH_3). They also reported that a stable uranium nitride $UN_{1.90\pm0.02}$ could be prepared by the reaction of UF_4 with a stream of NH_3. Katsura et al. reported the formation of $UN_{>1.80}$ using flowing NH_3 below 600°C [5–7]. All these results suggest that uranium nitrides with N/U atom ratios >1.80 can be obtained only by the action of high nitrogen pressure or by use of NH_3.

Equilibrium N_2 pressure–temperature–composition (P–T–C) relationships have been obtained by equilibrating α-U_2N_{3+x} prepared by the reaction between U and N_2 with N_2 gas [8,9,11–13]. Lapat and Holden, as well as Bugl and Bauer, calculated the partial molar enthalpy $\Delta\overline{H}$ and partial molar entropy $\Delta\overline{S}$ for the solution of nitrogen in α-U_2N_{3+x} with low nitrogen content (N/U<1.68) which was obtained by the reaction of U with N_2 [8,9]. Serizawa et al. estimated $\Delta\overline{H}$ and $\Delta\overline{S}$ values for the solution of α-U_2N_{3+x} with N/U ratios >1.78 by the reaction of UH_3 with a mixture of NH_3 and H_2 [10]. However, available data for $\Delta\overline{H}$ and $\Delta\overline{S}$ for the solution of nitrogen in α-U_2N_{3+x} with N/U ratios 1.68–1.77 are lacking, as it is difficult to obtain P–T–C relationship for this region. This may be due to the fact that the nitrides having N/U≥1.70 cannot be obtained by the reaction of U with N_2 under normal pressures. Urabe et al. overcame this difficulty by using nitrogen-rich α-U_2N_{3+x} prepared by reaction of U with NH_3 as a starting material and obtained the P–T–C relationship at 400, 600 and 800°C [14]. In the present work, in addition to the above three temperatures, the isotherms at 500, 700 and 900°C are measured. Based on these data, $\Delta\overline{H}$ and $\Delta\overline{S}$ values for the solution of nitrogen in α-U_2N_{3+x} with N/U rations 1.63–1.76 are estimated. Free energies for the solution of nitrogen in α-U_2N_{3+x} are also obtained.

2. Experimental

Metallic uranium, about 0.2 g in the form of a chip, was abraded with emery paper soaked in xylene and leached in 6 N HNO_3 for 2 h. The bright metal thus prepared was weighed in a quartz boat and inserted into the reaction tube filled with N_2 gas. The system was then evacuated to the

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order of 10^{-5} Pa at room temperature. Thereafter hydrogen was admitted into the reaction tube to about 80 kPa, and the uranium metal was hydrided at 225°C to form UH_3 powder. The temperature was raised to about 600°C to decompose the hydride to uranium metal powder and H_2 gas. The hydriding and dehydriding steps were repeated several times in order to ensure that all the uranium was converted to a fine powder. After the uranium powder was hydrided again at 225°C, the system was evacuated. An ammonia gas stream (150 ml min^{-1}) was supplied to the reaction tube and the temperature was raised to 600°C. The sample was kept at this temperature for an hour in order to form the single α-U_2N_{3+x} phase. The temperature was then lowered to 300°C and kept for 20 h to obtain a high nitrogen content α-U_2N_{3+x} (N/U>1.80). Afterwards the system was cooled to room temperature, and was evacuated to the order of 10^{-5} Pa. Nitrogen gas was then introduced into the system either to about 1.3 kPa or to about 13 kPa and the temperature was again raised to the desired value in the range from 400 to 900°C. In addition, experiments attaining the desired temperature without introduction of N_2 at room temperature were performed. Nitrogen-rich α-U_2N_{3+x} as the starting material evolved N_2 until equilibrium had been reached. The pressure of nitrogen, P_{N_2}, was measured for 40–400 h, and the establishment of equilibrium was judged by following the variation of P_{N_2} with time. When P_{N_2} remained constant for over 20 h, equilibrium was assumed to be reached. After the equilibrium nitrogen pressure was determined, the specimen was quickly cooled to room temperature and subjected to X-ray diffraction analysis (XRD). The XRD patterns of the samples were obtained at room temperature with a diffractometer (Rigaku Denki, Geiger Flex RAD-rA) using crystal monochromatized Cu Kα radiation. The lattice parameter of α-U_2N_{3+x} was calculated by Cohen's method using silicon as an external calibration. N/U atom ratios were estimated from the lattice parameter–composition relationship reported by Tagawa [15].

3. Results and discussion

Fig. 1 shows the equilibrium nitrogen pressure–temperature–composition relationship obtained in this work. The N/U ratio of the α-U_2N_{3+x} samples used as starting materials is greater than 1.80 and thermodynamically is very unstable. The difference between the chemical potential of nitrogen in the starting material and that of equilibrium α-U_2N_{3+x} may be extremely large and, hence, a high driving force toward equilibrium may be expected.

The equilibrium examined in the present work can be written as

$$\alpha\text{-}U_2N_{3+x+\Delta x} = \alpha\text{-}U_2N_{3+x} + \frac{\Delta x}{2}N_2 \tag{1}$$

This equation states that $\Delta x/2$ mol of nitrogen leaves α-$U_2N_{3+x+\Delta x}$ and forms α-U_2N_{3+x}. At equilibrium the free energies of both sides of Eq. (1) are set equal, so the following relation is readily obtained:

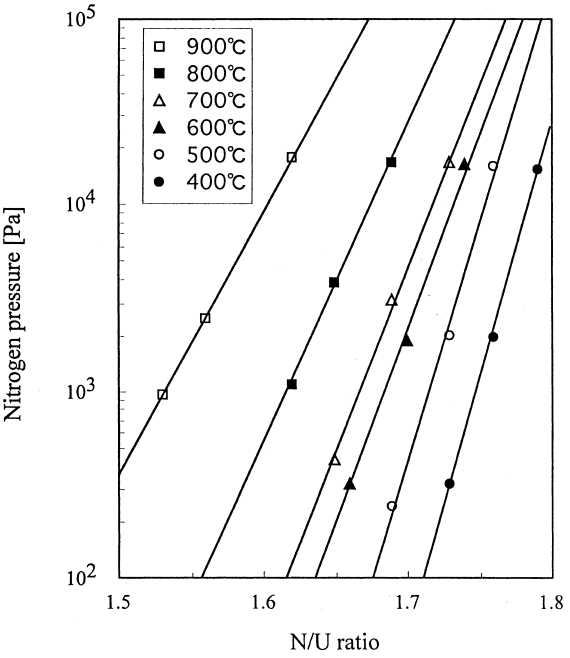

Fig. 1. Equilibrium nitrogen pressure of α-U_2N_{3+x} as a function of the composition at different temperatures.

$$\Delta G^{\circ}_{f,U_2N_{3+x+\Delta x}} = \Delta G^{\circ}_{f,U_2N_{3+x}} + \frac{\Delta x}{2}RT\ \ln(P_{N_2}) \tag{2}$$

where $\Delta G^{\circ}_{f,U_2N_{3+x+\Delta x}}$ and $\Delta G^{\circ}_{f,U_2N_{3+x}}$ are the standard free energies for formation of α-$U_2N_{3+x+\Delta x}$ and α-U_2N_{3+x}, respectively. The relation expressing true equilibrium is obtained by the condition $\Delta x \rightarrow 0$. Using Taylor's expansion and retaining only the first-order term in the limit $\Delta x \rightarrow 0$, the left-hand term of Eq. (2) is given by

$$\Delta G^{\circ}_{f,U_2N_{3+x+\Delta x}} = \Delta G^{\circ}_{f,U_2N_{3+x}} + \frac{\partial \Delta G^{\circ}_{f,U_2N_{3+x}}}{\partial x}\Delta x \tag{3}$$

Rearranging by substituting Eq. (3) into Eq. (2), the following equation is obtained:

$$\frac{\partial \Delta G^{\circ}_{f,U_2N_{3+x}}}{\partial x} = \frac{1}{2}RT\ \ln(P_{N_2}) \tag{4}$$

The left-hand side of Eq. (4) is, by definition, the partial molar free energy $\Delta\overline{G}$ for the solution of nitrogen into α-U_2N_{3+x}. As $\Delta\overline{G}$ is given by

$$\Delta\overline{G} = \Delta\overline{H} - T\Delta\overline{S} \tag{5}$$

one obtains from Eqs. (4) and (5)

$$\ln(P_{N_2}) = \frac{2\Delta\overline{H}}{R}\frac{1}{T} - \frac{2\Delta\overline{S}}{R} \tag{6}$$

By plotting the natural logarithm of the nitrogen pressure

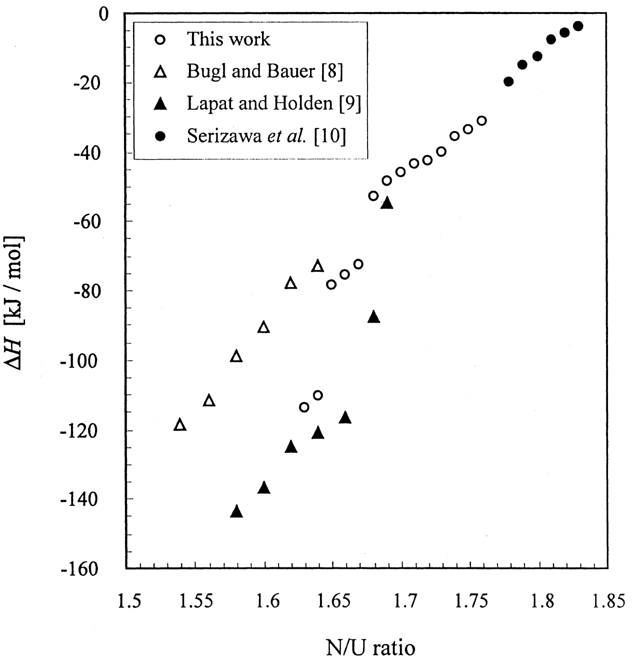

Fig. 2. Partial molar enthalpy for nitrogen solution in α-U_2N_{3+x} versus N/U atom ratio for the present and other measurements reported in the literature.

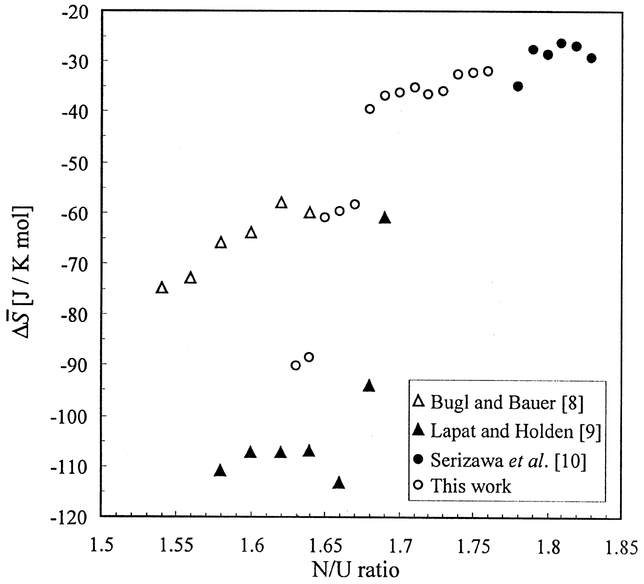

Fig. 3. Partial molar entropy for nitrogen solution in α-U_2N_{3+x} versus N/U atom ratio for the present and other measurements reported in the literature.

versus $1/T$, the plot is a straight line, and the slope and the interception are $2\Delta\overline{H}/R$ and $-2\Delta\overline{S}/R$, respectively.

Fig. 2 shows $\Delta\overline{H}$ versus the N/U atom ratio together with the available reported data for various N/U ratios [8–10]. In this work, the relationship between $\Delta\overline{H}$ and α-U_2N_{3+x} composition in the range 1.63–1.76 was obtained. Serizawa et al. suggested a biquadratic fit curve connecting the data of Bugl and Bauer with theirs [10]. There was no theoretical justification for using the biquadratic fit function. Despite no phase change of α-U_2N_{3+x} in the composition range 1.65<1.85 [16], an abrupt change in $\Delta\overline{H}$ around N/U=1.68 is found in the results of Lapat and Holden. Therefore, Serizawa et al. favored the results of Bugl and Bauer because the change in $\Delta\overline{H}$ between the data of Bugl and Bauer and that of Serizawa et al. seemed continuous. As seen in Fig. 2, the present author's new data in the lower nitrogen content region approach the results of Lapat and Holden rather than those of Bugl and Bauer. Fig. 3 shows the $\Delta\overline{S}$ versus N/U atom ratio obtained in this work and reported previously [8–10]. $\Delta\overline{S}$ values in the higher nitrogen content region obtained in this work are also in agreement with the data of Serizawa et al. The three measurements (this paper and Refs. [8,9]) of $\Delta\overline{S}$ in the lower nitrogen content region contradict each other. It is just a guess that the discrepancy among these $\Delta\overline{H}$ and $\Delta\overline{S}$ values in the N/U<1.7 region could be due to the different experimental methods or the presence of oxide impurities in the nitrides. In order to resolve this problem, further detailed experiments are required.

Fig. 4 shows the value of $\Delta\overline{G}$ calculated using Eq. (4) and the present data, in which the dependence of $\Delta\overline{G}$ on N/U is shown at several temperatures. The figure indicates a linear increase in $\Delta\overline{G}$ with increasing N/U ratio. $\Delta\overline{G}=0$ corresponds to a nitrogen pressure of 1 bar. This suggests that α-U_2N_{3+x} with a composition above 1.73 cannot be prepared theoretically by the reaction of uranium with 1 bar nitrogen at 900°C. The same can be said for N/U>

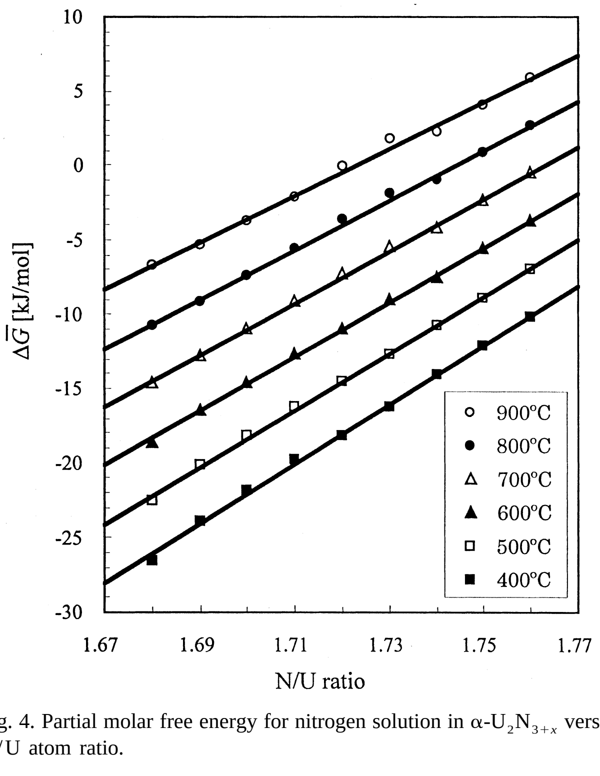

Fig. 4. Partial molar free energy for nitrogen solution in α-U_2N_{3+x} versus N/U atom ratio.

1.75 at 800°C and >1.77 at 700°C. To obtain α-U_2N_{3+x} with N/U atom ratio 1.75 by the reaction of uranium with N_2 at 900°C, a N_2 pressure of about 2.3 bar is necessary.

4. Conclusions

The nitrogen pressure–composition isotherms for the α-U_2N_{3+x} phase were obtained in the temperature range from 400 to 900°C by equilibrating nitrogen-rich α-U_2N_{3+x} with an N/U atom ratio greater than 1.80 prepared by the reaction of U with flowing NH_3. Using these isotherms the thermodynamic properties (partial molar enthalpy, entropy and free energy for solution of nitrogen) of α-U_2N_{3+x} with N/U atom ratio 1.63–1.76 were obtained.

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