DTA MEASUREMENTS IN THE URANIUM-NITROGEN SYSTEM

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ABSTRACT

DTA-measurements were carried out to obtain some additional data on the phase relations in the U-N system. The nitrogen decomposition pressure of $\beta$-$U_2N_3$ and $UN_{1.5}O_2(1-z)$, as well as the equilibrium nitrogen pressure for the reaction from $\beta$- to $\alpha$-$U_2N_3$ were measured as a function of temperature.

1. The temperature dependence of the equilibrium nitrogen pressure for the reaction: $2UN + \frac{1-z}{2}N_2 \rightleftharpoons \beta-U_2N_3 - x$, measured by DTA, showed a fairly good agreement with the results obtained by other methods and is expressed by the equation:

$$\log P_{N_2} (\text{atm}) = 6.361 - 10.649 \times 10^3/T (1450 - 1660 \text{ K})$$

i.e., $UN$ transforms to $\beta-U_2N_3$ at 1390°C and 1 atm. $N_2$.

2. The reaction temperature from $\beta$- to $\alpha$-$U_2N_3$ was examined at various nitrogen pressures. The equilibrium nitrogen pressure for the reaction:

$$\beta-U_2N_3 - x + \frac{x+y}{2}N_2 \rightleftharpoons \alpha-U_2N_3 + y$$

is:

$$\log P_{N_2} (\text{atm}) = 6.131 - 8.115 \times 10^3/T (1145 - 1325 \text{ K})$$

i.e., $\beta-U_2N_3$ transforms to $\alpha-U_2N_3$ at 1050°C and 1 atm. $N_2$.

3. When oxygen is dissolved in the $\alpha$-phase, the nitrogen decomposition pressure of $UN_{1.5}O_2(1-z)$ to $\beta-U_2N_3$ (in the case of low oxygen content), or to $UN$ (high oxygen content) becomes lower than that of pure $\alpha-U_2N_3$.

Such a reduction of the nitrogen potential can be useful to suppress the fuel-cladding interaction in a nitride fuel element at high burn-up.
INTRODUCTION

The knowledge of phase relations and thermodynamic data in the uranium-nitrogen system is important, because of the potential of (U,Pu)N as a nuclear fuel. The thermodynamical properties in the U$_2$N$_3$ region have not been so well established as those in the U-UN region, in spite of its technical importance for understanding the burn-up behaviour of a nitride fuel. Four compounds are known in this system, UN, a-U$_2$N$_3$, ß-U$_2$N$_3$ and UN$_2$, which have the crystal structure of fcc NaCl type, bcc Mn$_2$O$_3$ type, hcp La$_2$O$_3$ type and fcc CaF$_2$ type, respectively. The homogeneity range of UN is very narrow even at high temperature (1). a-U$_2$N$_3$ contains more nitrogen than is indicated by its formula (2,3,4) and exhibits a wide homogeneity range. ß-U$_2$N$_3$ is the high temperature phase with lower N/U composition than 1.5 (5,6,7,8) and is reported to be stable above about 800°C (1,8). The decomposition nitrogen pressures of UN and ß-U$_2$N$_3$ have been investigated several times, but there is no measurement of equilibrium nitrogen pressure for the reaction a + 2N$_2$. In this study, at first, the reaction temperature of a ß as well as that of UN ß a-U$_2$N$_3$ were measured by DTA method under various nitrogen pressures.

With respect to the nitrogen potential the a-U$_2$N$_3$ phase is stabilized by the presence of oxygen, dissolved in the nitride phase (1,10,11). At low temperatures oxygen solubility in the a-U$_2$N$_3$ phase is low. At elevated temperature there is a complete miscibility between UO$_2$ and a-U$_2$N$_3$ (5). This compound retains the a-U$_2$N$_3$ structure at least up to 60 mol.% UO$_2$ and has a larger lattice parameter than pure a-U$_2$N$_3$. In this work the equilibrium nitrogen pressure of the U$_2$N$_3$ phase with various oxygen contents was measured. This has a technical importance in respect to the compatibility problem of nuclear fuel with cladding material. The stability of ß-U$_2$N$_3$ with small intake oxygen was also examined.

EXPERIMENTAL

1. DTA measurements

The high temperature DTA apparatus by Netzsch co. was used to observe the reaction temperature under various nitrogen pressures. The sample holder and reference material was alumina. Measurements were carried out between room temperature and 1550°C with the heating and cooling rate of 10°C/min. either in a gas stream of pure nitrogen, pure argon, mixtures of
both, or in a closed system with a certain pressure of pure nitrogen. The accuracy of the temperature measurement by the Pt-PtRh thermocouple, which was calibrated by the melting points of Ag (960°C) and NaCl (800°C), was within ± 5°C.

When the differential temperature is plotted against the surface temperature of the sample, the point of initial departure from the baseline of the DTA curve should correspond to the reaction temperature (12). Therefore in this experiment the onset points which are indicated by arrows in Fig.1, should be regarded as the reaction temperatures.

2. Sample preparation

UN powder (O₂ < 1000 ppm) was used for the study of the pure uranium-nitrogen system and as starting material to form the oxynitride. For the preparation of the oxynitrides, the powders of U₂N₃ and UO₂ were mixed, cold-pressed and homogenized in 300 Torr nitrogen at 1700°C for 3 hrs. and then at 1550°C for 15 hrs. These samples were examined by X-ray and chemical analysis for composition and phases present.

RESULTS

A typical heating and cooling curve of DTA for the pure uranium nitride is shown in Fig.1a. The four peaks in the curve correspond to the following reactions:

(A 1) \( a-U₂N₃ + xN₂ \rightarrow \beta-U₂N₃ + xN₂ \)

(A 1') \( a-U₂N₃ + xN₂ \rightarrow \beta-U₂N₃ + xN₂ \)

(A 2) \( 2UN + \frac{1}{2}N₂ \rightarrow \beta-U₂N₃ \)

(A 2') \( 2UN + \frac{1}{2}N₂ \rightarrow \beta-U₂N₃ \)

For these reactions, the relation between reaction temperature and nitrogen pressure is shown in Fig.2. The white and black circles correspond to the onset temperature of the reaction peak A 2 (heating cycle) and A 2' (cooling cycle), respectively. The reaction temperature on both cycles agreed well and the relation, which is calculated by the least squares method, is:

\[
\log P_{N₂} (\text{atm}) = 6.361 - 10.649 \times \frac{10^3}{T} (1450 - 1660 K)
\]  

(1)

In the case of reaction A 1, the nitrogen pressure dependence of the reaction temperature was not clear. On the reverse reaction, however, there is a clear relation which is expressed by the equation:

\[
\log P_{N₂} (\text{atm}) = 6.131 - 8.115 \times \frac{10^3}{T} (1145 - 1325 K)
\]  

(2)
In order to investigate the influence of oxygen on the reaction temperature, up to 10 vol.\% of oxygen gas was mixed with the nitrogen gas. The DTA measurement was carried out in a closed system with a total pressure of 1 atm. At first, the increase of the reaction temperature and the decrease of the reaction intensities were observed for all the existing peaks and a pair of additional peaks appeared at high temperature as shown in Fig.1b. Temperatures of the reactions with and without oxygen are listed in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction temperature at 1 atm N₂</th>
<th>without oxygen gas</th>
<th>with 10 vol.% oxygen gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>β + N₂ → α</td>
<td>1050°C</td>
<td>1180°C</td>
<td></td>
</tr>
<tr>
<td>α + β + N₂</td>
<td>1205°C</td>
<td>1290°C</td>
<td></td>
</tr>
<tr>
<td>β₂ + UN</td>
<td>1390°C</td>
<td>1465°C</td>
<td></td>
</tr>
</tbody>
</table>

These results show that the β phase, as well as the α phase, can dissolve oxygen. The influence of oxygen was further investigated quantitatively.

The results of the DTA measurements of samples with definite oxygen contents are presented in Table 2. The schematic DTA curve of the homogenized oxynitride is shown in Fig.1c. The relative intensities of the peaks and the reaction temperatures are strongly dependent on the oxygen content. The DTA peaks were identified as the following reactions.

\[(B\ O): (1-z) UO₂ + \frac{z}{2} U₂N₃ \Leftrightarrow UN_{1.52}O_{2(1-z)}\]

This reversible reaction is a dissociation-formation reaction of the oxynitride. The reaction temperatures of both cooling (dissociation) and heating (formation) cycles were the same and independent of nitrogen pressure. We observed: 1130 ± 20°C for UN₁₋₀.₆₄ and 1150 ± 20°C for UN₁₋₀.₇₁. Because of the rapid reaction, the UN₁₋₀.₅₂ phase could not be quenched.

\[(B\ I): α(α) + β(α) + α'(α) + N₂\]

α(α), α'(α): UN₁₋₀.₅₂(1-z) with different z values

β(α) : β = U₂N₃ phase including oxygen
The change of the reaction temperature with increasing oxygen content which is already shown in Table 1, lends further support to the existence of an oxygen solubility in the β phase.

\[ \beta(o) + a'(o) \not\iff UN + a''(o) + N_2 \]

β-U₂N₃ was stabilized by oxygen with respect to decomposition into UN and N₂. Below 1300°C the stability seems to be proportional to the total oxygen content in the sample, as shown in Fig. 3. At temperatures above about 1400°C the samples with various oxygen contents show the same decomposition pressure. This can be explained by a constant but higher oxygen content in the β phase, taking part in the reaction.

\[ a''(o) \iff UN + UO₂ + N_2 \]

Figure 3 shows that the decomposition nitrogen pressure of the oxinitride a''(o) is lowered with increasing oxygen content. In the case of large oxygen content, the β-phase does not exist and the α phase decomposes directly to UN, UO₂ and N₂.

**DISCUSSION**

1. Decomposition nitrogen pressure of α- and β-U₂N₃

   For the reaction β-U₂N₃ \iff UN + 2N₂ experimental results of the equilibrium nitrogen pressure by many investigators are shown in Fig. 4. The results by DTA showed a good agreement with those obtained from other methods using effusion cell (13), thermobalance (3), Sievert apparatus (2) and manometer (4, 14). In the reaction α-U₂N₃ \iff β-U₂N₃ + yN₂, the nitrogen pressure of decomposition of α-U₂N₃ must be distinguished from that of formation. Disagreement of the reaction temperature between heating and cooling cycles may be attributed to the reaction mechanism. Such a hysteresis of the reaction is frequently observed in the "nucleation and growth" transformations. It is conceivable that the nucleation process is affected by the oxygen impurity. This could be a cause for the fluctuation of the reaction temperature for the reaction from α-U₂N₃ to β-U₂N₃.

2. Oxinitride

2-1) The composition of the oxinitrides

The content of oxygen and nitrogen determined in oxinitrides are plotted in Fig. 5. The composition of our samples agreed reasonably well with the
formula \( UN_{1.5z}O_{2(1-z)} \), which is essentially the same as that proposed by Blum et al (11).

\[
2-2) \quad 1-z \text{UO}_2 + \frac{z}{2} \text{UN}_2 + \text{UN}_{1.5z}O_{2(1-z)}
\]

The reaction temperature by the present DTA measurements agreed very well with that obtained from X-ray measurements by Keller (15) and Blum et al (16). The temperature of this reaction was found to be independent of nitrogen pressure between \(3 \times 10^{-2}\) and 1 atm. This suggests that the reaction equation does not include a nitrogen molecule.

\[
2-3) \quad \alpha(o) + a'(o) + \beta(o) + N_2 + a''(o) + UN + N_2 + UN + UO_2 + N_2
\]

For the samples with small oxygen content, these reactions were identified from the DTA curve. Although these reactions are essentially the same with those described by Benz et al (5), it should be pointed out that the \( \beta \) phase also exhibited an oxygen solubility.

In the first reaction the broadening of the DTA peak with oxygen is plausible, because the dissociation reaction of the oxynitride is connected with a continuous change in composition of the \( \alpha' \) phase. In view of the results in Fig.3, the oxygen solubility at high temperature in \( \beta-U_2N_3 \) is considered to be at most 2 atomic %.

3. Compatibility

The \( U_2N_3 \) formation and the increase of nitrogen pressure due to the burn-up of a nitride fuel will cause an unfavorable effect with regard to compatibility with the cladding material. It is probable that by dispersing a small amount of \( \text{UO}_2 \) in the UN fuel in advance, \( U_2N_3 \) formed during burn-up will react with \( \text{UO}_2 \) and form an oxynitride. The formation of this oxynitride is expected to contribute to a decrease of nitrogen potential in the fuel.

Although we cannot draw a clear conclusion whether the formation of oxynitride can prevent a reaction between \( U_2N_3 \) and Cr -the most critical component concerning nitride formation in case of stainless steel as cladding material- the decrease of nitrogen potential due to the presence of the oxynitride can be useful to suppress the fuel-cladding interaction. The real compatibility problem should be solved by investigating the direct reaction between oxygen containing nitride fuel and the cladding material.
REFERENCES

(3) P. E. Lapat and R. B. Holden, ibid. p. 225 (1964)
(15) D. L. Keller, BMI - 1872 (1969)
Table 2: Results of the DTA measurements for the oxynitrides at nitrogen pressures of 1.0 and 0.1 atm.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>UN_{m}O_{n}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(m)</td>
<td>(n)</td>
<td></td>
</tr>
<tr>
<td>1)</td>
<td>1.505</td>
<td>0.018</td>
</tr>
<tr>
<td>2)</td>
<td>1.492</td>
<td>0.056</td>
</tr>
<tr>
<td>3)</td>
<td>1.404</td>
<td>0.106</td>
</tr>
<tr>
<td>4)</td>
<td>1.340</td>
<td>0.225</td>
</tr>
<tr>
<td>5)</td>
<td>1.250</td>
<td>0.380</td>
</tr>
<tr>
<td>6)</td>
<td>1.146</td>
<td>0.465</td>
</tr>
<tr>
<td>7)</td>
<td>0.997</td>
<td>0.640</td>
</tr>
<tr>
<td>8)</td>
<td>0.710</td>
<td>1.066</td>
</tr>
</tbody>
</table>

Note a) For example [(0.1) 1130] means the reaction temperature of 1130°C at 0.1 atm nitrogen pressure
b) This temperature indicates reaction from β- to α-\(\text{U}_2\text{N}_3\)
c) \(\alpha'(0)\) and \(\alpha''(0)\) are bcc \(\alpha-\text{U}_2\text{N}_3\) containing oxygen and \(\beta(0)\), hcp \(\beta-\text{U}_2\text{N}_3\) containing oxygen
Fig. 1: Heating-cooling cycle of the DTA curve in the uranium-nitrogen system

a. without oxygen,
b. with low oxygen content,
c. with high oxygen content (schematic)
Fig. 2: Equilibrium nitrogen pressure for the reactions:

\[ \begin{align*}
\beta - \text{U}_2\text{N}_3 - x & \rightarrow 2 \text{UN} + \frac{1-x}{2} N_2; \quad 2 \text{UN} + \frac{1-x}{2} N_2 \rightarrow \beta - \text{U}_2\text{N}_3 - x; \\
\alpha - \text{U}_2\text{N}_3 + y & \rightarrow \beta - \text{U}_2\text{N}_3 - x + \frac{x+y}{2} N_2 \quad \text{and} \quad \beta - \text{U}_2\text{N}_3 - x + \frac{x+y}{2} N_2 \rightarrow \alpha - \text{U}_2\text{N}_3 + y
\end{align*} \]
Fig. 3: Nitrogen decomposition pressure of $\beta$-U$_2$N$_3$ (open symbols) and $\alpha$-U$_2$N$_3$ (closed symbols) in samples with various oxygen contents.
Fig. 4: Nitrogen decomposition pressure of $\beta$-U$_2$N$_3$
Fig. 5: The composition of the oxynitrides $UN_{n}O_{m}$

- Theoretical formula $UN_{1.5z}O_{2(1-z)}$
- Benz et al.
- Leitnaker et al.
- This work