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 β-U_2N_3 and $UN_{1.5z}O_{2(1-z)}$ $(0 \leqslant z \leqslant 1)$ as well as the equilibrium nitrogen pressure for the reaction from β- to α-U_2N_3 was measured as a function of temperature.

1. The temperature dependence of the equilibrium nitrogen pressure for the reaction: $2UN + \frac{1-x}{2} N_2 \rightleftarrows \beta$-$U_2N_{3-x}$, measured by DTA, showed a fairly good agreement with the results obtained by other methods and is expressed by the equation:
   $$\log P_{N_2} \text{ (atm.)} = 6.361 - 10.649 \times 10^3/T \quad (1450 - 1660^\circ K)$$
   i.e., UN transforms to β-U_2N_3 at $1390^\circ C$ and 1 atm. N_2.

2. The reaction temperature from β- to α-U_2N_3 was examined at various nitrogen pressures. The equilibrium nitrogen pressure for the reaction
   $$\beta\text{-}U_2N_{3-x} + \frac{x+y}{2} N_2 \rightarrow \alpha\text{-}U_2N_{3+y} \text{ is:}$$
   $$\log P_{N_2} \text{ (atm.)} = 6.131 - 8.115 \times 10^3/T \quad (1145 - 1325^\circ K)$$
   i.e., β-U_2N_3 transforms to α-U_2N_3 at $1050^\circ C$ and 1 atm. N_2

3. When oxygen is dissolved in the α-phase, the nitrogen decomposition pressure of $UN_{1.5z}O_{2(1-z)}$ to β-U_2N_3 (in the case of low oxygen content), or to UN (high oxygen content) becomes lower than that of pure α-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_2N_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, α-U_2N_3, β-U_2N_3 and UN_2, which have the crystal structure of fcc NaCl type, bcc Mn_2O_3 type, hcp La_2O_3 type and fcc CaF_2 type, respectively. The homogeneity range of UN is very narrow even at high temperature (1). α-U_2N_3 contains more nitrogen than is indicated by its formula (2,3,4) and exhibits a wide homogeneity range. β-U_2N_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 β-U_2N_3 have been investigated several times, but there is no measurement of equilibrium nitrogen pressure for the reaction $\alpha \overset{\rightarrow}{\rightleftarrows} \beta + yN_2$. In this study, at first, the reaction temperature of $\alpha \overset{\rightarrow}{\rightleftarrows} \beta$ as well as that of UN $\overset{\rightarrow}{\rightleftarrows} \beta$-$U_2N_3$ were measured by DTA method under various nitrogen pressures.

With respect to the nitrogen potential the α-U_2N_3 phase is stabilized by the presence of oxygen, dissolved in the nitride phase. (1,10,11). At low temperatures oxygen solubility in the α-U_2N_3 phase is low. At elevated temperature there is a complete miscibility between UO_2 and α-U_2N_3 (5). This compound retains the α-U_2N_3 structure at least up to 60 mol.% UO_2 and has a larger lattice parameter than pure α-U_2N_3. In this work the equilibrium nitrogen pressure of the U_2N_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 β-U_2N_3 with small intake $\overset{of}{}$ 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
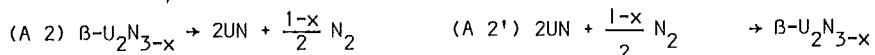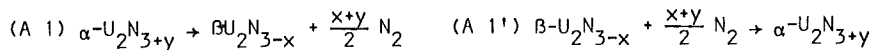within $\pm$ 5°C.

When the differential temperature is plotted against the surface tem-
perature of the sample, the point of initial departure from the base line
of the DTA curve should correspond to the reaction temperature (12). There-
fore 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 (O_2 < 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 U_2N_3 and UO_2 were mixed,
cold-pressed and homogenized in 300 Torr nitrogen at 1700°C for 3 hrs. and
then at 1550°C for 13 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) $\alpha\text{-}U_2N_{3+y} \rightarrow \beta U_2N_{3-x} + \frac{x+y}{2} N_2$ (A 1') $\beta\text{-}U_2N_{3-x} + \frac{x+y}{2} N_2 \rightarrow \alpha\text{-}U_2N_{3+y}$

(A 2) $\beta\text{-}U_2N_{3-x} \rightarrow 2UN + \frac{1-x}{2} N_2$ (A 2') $2UN + \frac{1-x}{2} N_2 \rightarrow \beta\text{-}U_2N_{3-x}$

For these reactions, the relation between reaction temperature and nitro-
gen 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:

$$\log P_{N_2} \text{ (atm) } = 6.361 - 10.649 \times 10^3/T \quad (1450 - 1660^\circ\text{K}) \qquad (1)$$

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

$$\log P_{N_2} \text{ (atm) } = 6.131 - 8.115 \times 10^3/T \quad (1145 - 1325^\circ\text{K}) \qquad (2)$$

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.

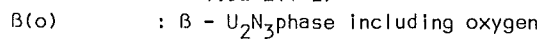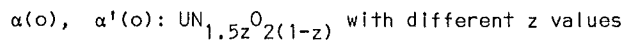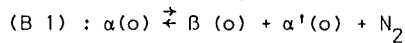Table 1:   Influence of oxygen on the reaction temperature

Reaction	Reaction temperature at 1 atm N_2	
	without oxygen gas	with 10 vol.% oxygen gas
$\beta + N_2 \rightarrow \alpha$	$1050^\circ C$	$1180^\circ C$
$\alpha \rightarrow \beta + N_2$	$1205^\circ C$	$1290^\circ C$
$\beta \rightleftharpoons UN$	$1390^\circ C$	$1465^\circ C$

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 schematical 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 0): $(1-z)$ UO_2 + $\frac{z}{2}$ U_2N_3 $\rightleftharpoons$ $UN_{1.5z}O_{2(1-z)}$
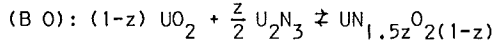
This reversible reaction is a dissociation-formation reaction of the oxynitride. The reaction temperatures of both cooling (dissociation) and heating (formation) cycles were the same and independent of nitrogen pressure. We observed: $1130 \pm 20^\circ C$ for $UN_{1.00}O_{0.64}$ and $1150 \pm 20^\circ C$ for $UN_{0.71}O_{1.07}$. Because of the rapid reaction, the $UN_{1.5z}O_{2(1-z)}$ phase could not be quenched.

(B 1) : $\alpha(o)$ $\rightleftharpoons$ β (o) + $\alpha'(o)$ + N_2

$\alpha(o)$, $\alpha'(o)$: $UN_{1.5z}O_{2(1-z)}$ with different z values

$\beta(o)$: β - U_2N_3 phase including oxygen

The change of the reaction temperature with increasing oxygen content
which is already shown in Table I, lends further support to the existence
of an oxygen solubility in the β phase.

(B 2): $\beta(o) + \alpha'(o) \rightleftarrows UN + \alpha''(o) + N_2$
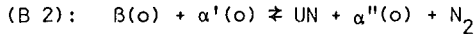
$\beta-U_2N_3$ was stabilized by oxygen with respect to decomposition into UN and
N_2. Below $1300^\circ C$ the stability seems to be proportional to the total oxy-
gen content in the sample, as shown in Fig.3. At temperatures above about
$1400^\circ C$ the samples with various oxygen contents show the same decomposi-
tion pressure. This can be explained by a constant but higher oxygen con-
tent in the β phase, taking part in the reaction.

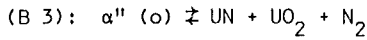(B 3): $\alpha''(o) \rightleftarrows UN + UO_2 + N_2$

Figure 3 shows that the decomposition nitrogen pressure of the oxinitride
$\alpha''(o)$ is lowered with increasing oxygen content. In the case of large oxy-
gen content, the β-phase does not exist and the α phase decomposes direct-
ly to UN, UO_2 and N_2.

DISCUSSION

1. Decomposition nitrogen pressure of α- and $\beta-U_2N_3$

For the reaction $\beta-U_2N_3 \rightleftarrows UN + zN_2$ 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 $\alpha-U_2N_3 \rightleftarrows \beta-U_2N_3 + yN_2$, the nitrogen pressure of de-
composition of $\alpha-U_2N_3$ must be distinguished from that of formation. Dis-
agreement 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" transforma-
tions. 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 $\alpha-U_2N_3$ to $\beta-U_2N_3$.

2. Oxynitride

2-1) The composition of the oxynitrides

The content of oxygen and nitrogen determined in oxynitrides 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) $1-z \ UO_2 + \frac{z}{2} U_2N_3 \rightleftarrows UN_{1.5z}O_{2(1-z)}$
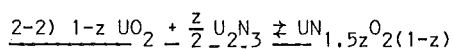
The reaction temperature by the present DTA measurements agreed very well with that obtained from X-ray measurements by Keller (15) and Blum et al (16). The temperature of this reaction was found to be independent of nitrogen pressure between 3×10^{-2} and 1 atm. This suggests that the reaction equation does not include a nitrogen molecule.

2-3) $\alpha(o) \rightarrow \alpha'(o) + \beta(o) + N_2 \rightarrow \alpha''(o) + UN + N_2 \rightarrow UN + UO_2 + N_2$
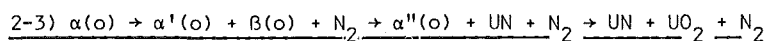
For the samples with small oxygen content, these reactions were identified from the DTA curve. Although these reactions are essentially the same with those described by Benz et al (5), it should be pointed out that the β phase also exhibited an oxygen solubility.

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 α' 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 UO_2 in the UN fuel in advance, U_2N_3 formed during burn-up will react with 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.

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Table 2: Results of the DTA measurements for the oxynitrides at nitrogen pressures of 1.0 and 0.1 atm.

	Composition UN_mO_n		Temperature $\longrightarrow$						
	(m)	(n)							
1)	1.505	0.018				(1.0) 1050[b] (0.1) 865 $\longleftrightarrow$	β	(1.0) 1390 (0.1) 1170 $\longleftrightarrow$	UN
2)	1.492	0.056	UO_2 $\longleftrightarrow$	unobserved	α (o)	(1.0) 1135 (0.1) not clear $\longleftrightarrow$	(c) α'(o) + β(o)	(1.0) 1460 (0.1) 1180 $\longleftrightarrow$ (1.0) 1460 (0.1) 1195 $\longleftrightarrow$ (1.0) 1460 (0.1) 1225 $\longleftrightarrow$	α"(o) + UN
3)	1.404	0.106	U_2N_3 + UO_2			not clear $\longleftrightarrow$			
4)	1.340	0.225				not clear $\longleftrightarrow$			
5)	1.250	0.380				$\longleftrightarrow$			
6)	1.146	0.465	not clear $\longleftrightarrow$			$\longleftrightarrow$			
7)	0.997	0.640	(1.0 and 0.1)[a] 1130 $\longleftrightarrow$			$\longleftrightarrow$			
8)	0.710	1.066	(1.0 and 0.1) 1150 $\longleftrightarrow$			$\longleftrightarrow$			

Right-hand columns (temperatures to UN / UO2 region):

(1.0) 1460 (0.1) 1220
(1.0) 1465 (0.1) 1225 → UN
(1.0) 1475 (0.1) 1235
(1.0) 1550 (0.1) 1255
(1.0) 1520 (0.1) 1265 → UO$_2$
(1.0) 1540 (0.1) 1280
(1.0) (0.1) unobs.

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-U_2N_3
c) α'(o) and α"(o) are bcc α-U_2N_3 containing oxygen and β(o), hcp β-U_2N_3 containing oxygen

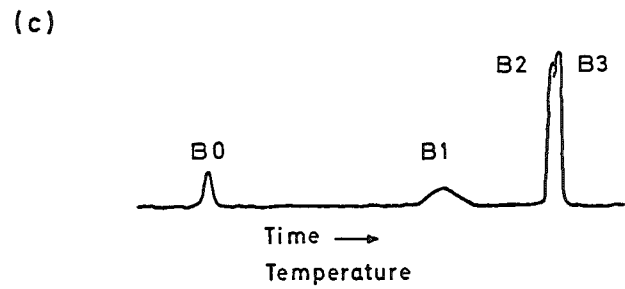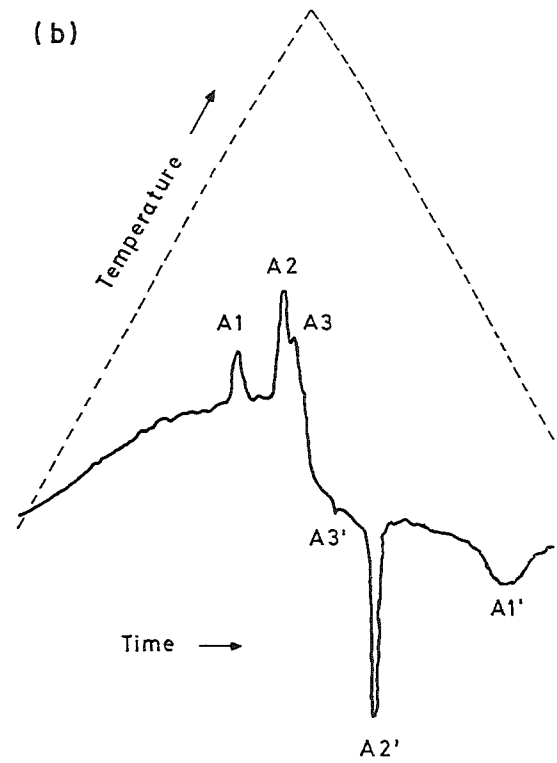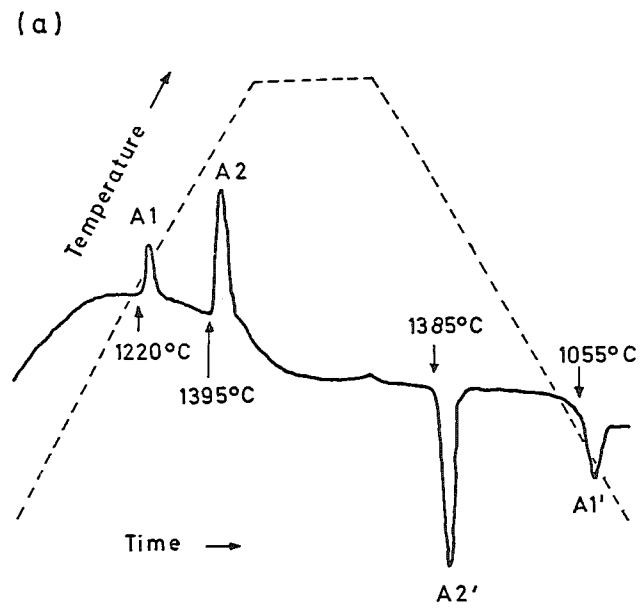Fig. 1: Heating-cooling cycle of the DTA curve in the uranium-
         nitrogen system
         a. without oxygen,
         b. with low oxygen content,
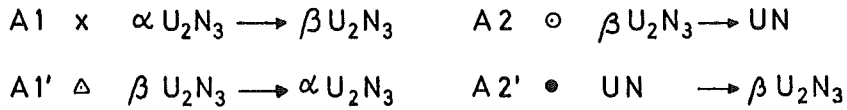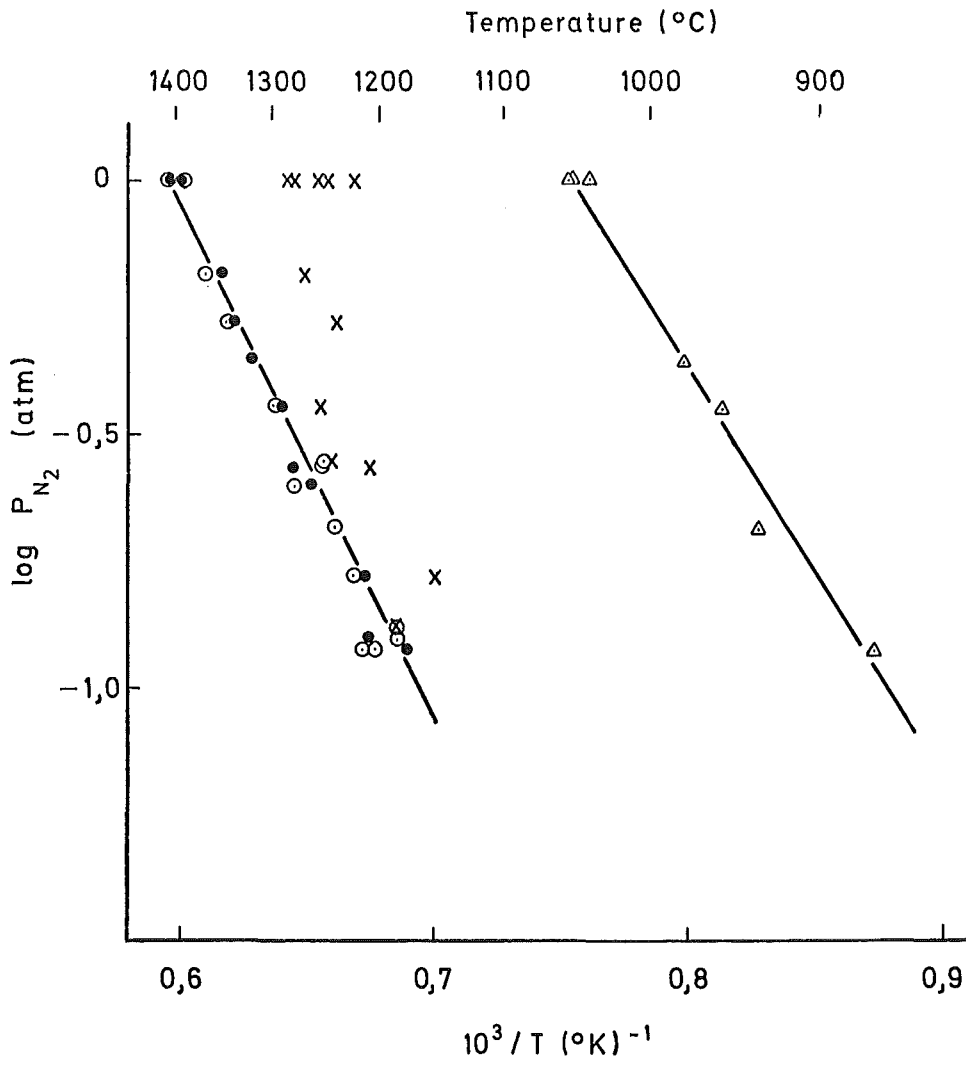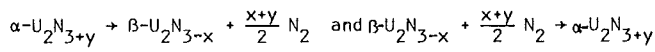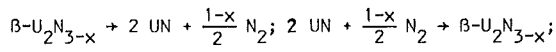   c. with high oxygen content (schematic)

Fig. 2: Equilibrium nitrogen pressure for the reactions:

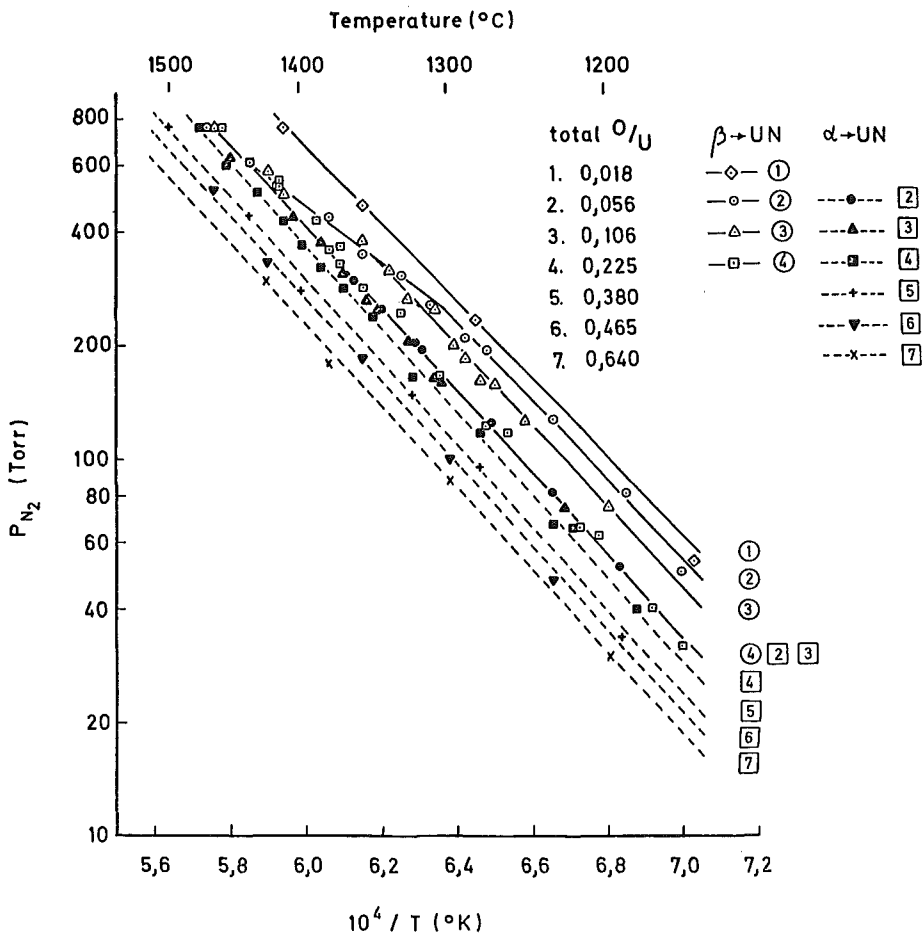$$\beta\text{-}U_2N_{3-x} \rightarrow 2\ UN + \frac{1-x}{2}\ N_2; \quad 2\ UN + \frac{1-x}{2}\ N_2 \rightarrow \beta\text{-}U_2N_{3-x};$$

$$\alpha\text{-}U_2N_{3+y} \rightarrow \beta\text{-}U_2N_{3-x} + \frac{x+y}{2}\ N_2 \quad \text{and}\ \beta\text{-}U_2N_{3-x} + \frac{x+y}{2}\ N_2 \rightarrow \alpha\text{-}U_2N_{3+y}$$

Temperature (°C)

1500   1400   1300   1200

P_{N_2} (Torr)

10^4 / T (°K)

total $O/_U$	$\beta \to UN$	$\alpha \to UN$
1. 0,018	—◇— ①	
2. 0,056	—○— ②	---●--- ②
3. 0,106	—△— ③	---▲--- ③
4. 0,225	—□— ④	---◙--- ④
5. 0,380		---+--- ⑤
6. 0,465		---▼--- ⑥
7. 0,640		---×--- ⑦

Fig. 3: Nitrogen decomposition pressure of β-U_2N_3 (open symbols) and α-U_2N_3 (closed symbols) in samples with various oxygen contents
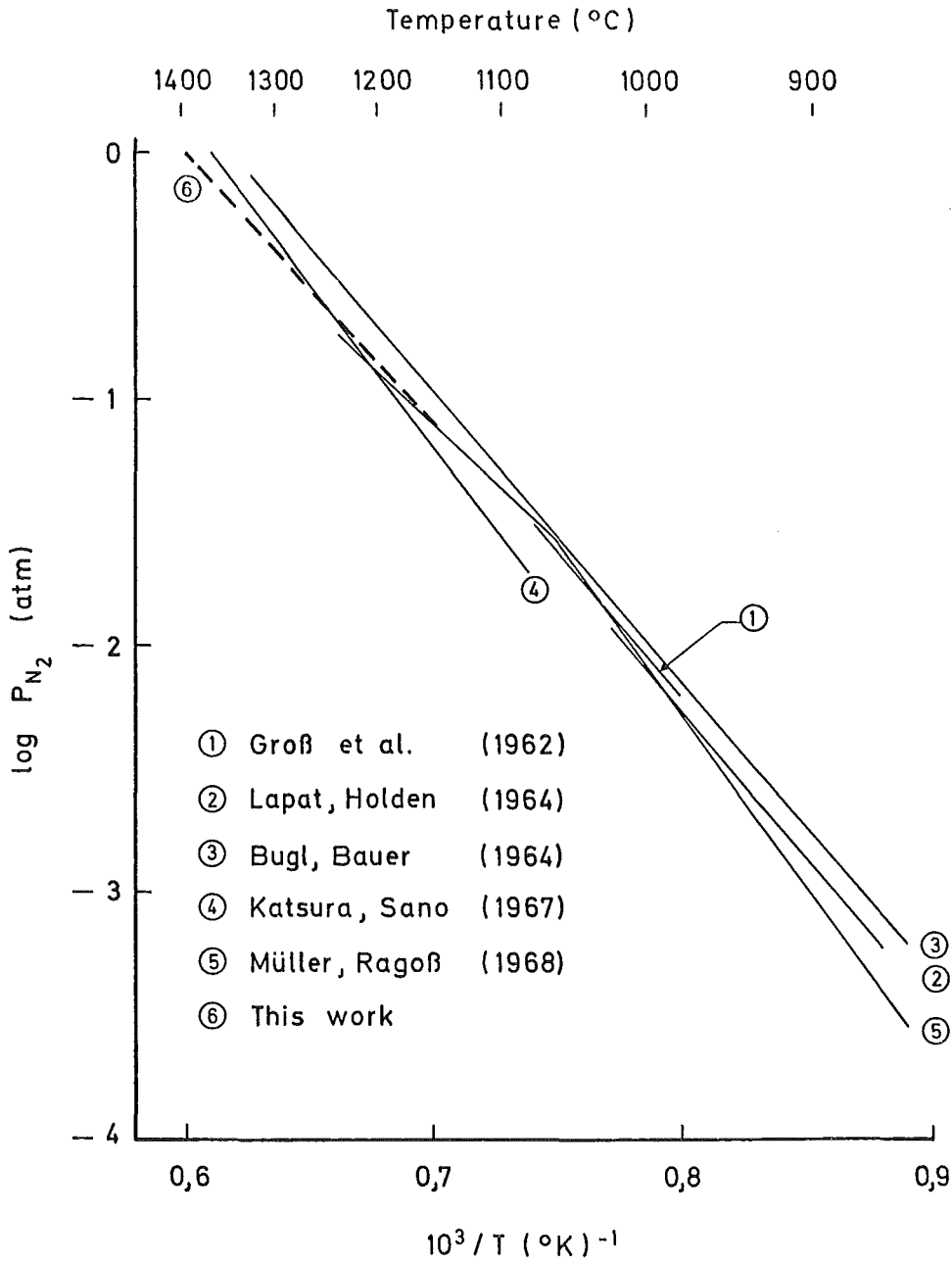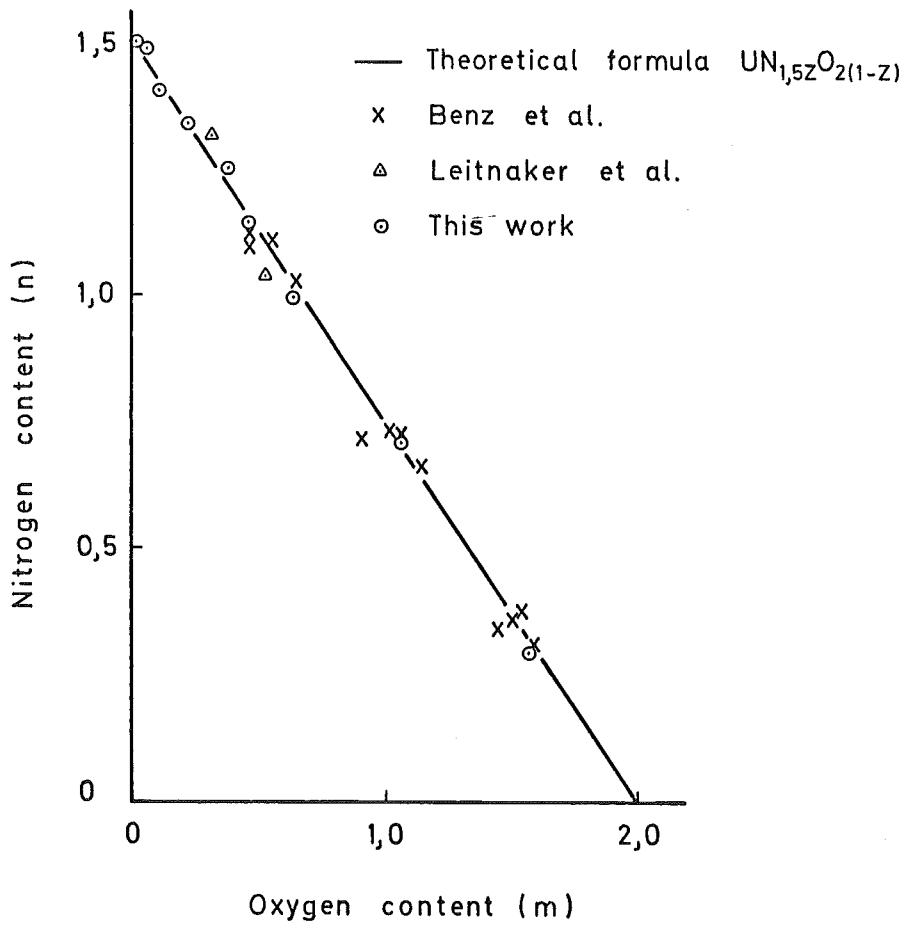
Temperature (°C)

Fig. 4: Nitrogen decomposition pressure of β-U_2N_3

Fig. 5: The composition of the oxynitrides UN_nO_m