Journal of Alloys and Compounds, 213/214 (1994) 440–443
JALCOM 4105

The role of unstable NH_3 in the formation of nitrogen-rich α-U_2N_{3+x} by the reaction of UC or U with NH_3

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Abstract

Reactions of U or UC with a stream of NH_3 or N_2 were carried out at 600 and 900 °C. It has been found that in high temperature reactions of U or UC with flowing NH_3, the catalytic decomposition of NH_3 proceeds in parallel with the nitridation reaction of U or UC by action of NH_3, which leads to the formation α-U_2N_{3+x}, and eventually a steady state is established where the partial pressures of NH_3, H_2 and N_2 (P_{NH_3}, P_{H_2}, and P_{N_2}) in the flowing gas and the N:U ratio of α-U_2N_{3+x} are all uniquely determined. The nitrogen activity a_N of the flowing gas may be increased by suppressing the decomposition of NH_3 into H_2 and N_2. The N:U ratio of α-U_2N_{3+x} increases as the extent of dissociation of NH_3, α, decreases.

1. Introduction

The dissociation of NH_3 into N_2 and H_2 can be suppressed well below its equilibrium dissociation degree under appropriate experimental conditions and in this case NH_3 must be considered to be in a thermodynamically unstable state with respect to the equilibrium $NH_3=\frac{1}{2}N_2+\frac{3}{2}H_2$. A large NH_3 gas flow may provide an excellent device for this purpose, in particular at high temperatures. Katsura [1] demonstrated that extremely high nitrogen activity a_N can be realized in gas phases consisting of unstable NH_3, N_2 and H_2 as prepared by keeping the extent of dissociation of NH_3 well below its equilibrium dissociation degree. It is generally admitted that α-uranium sesquinitride has a wide composition range towards UN_2 and this non-stoichiometric nitride is often written as α-U_2N_{3+x} ($0\leqslant x\leqslant 1$). The atomic ratio N:U of α-U_2N_{3+x} formed by the reaction of U with N_2 under normal pressures (1 bar or less) at temperatures of 600–900 °C never exceeds 1.75 [2, 3], while α-U_2N_{3+x} with an N:U ratio larger than 1.80 can be easily prepared by flowing NH_3 over a U sample held at 600–900 °C [4–8]. The formation of N-rich α-U_2N_{3+x}, which cannot be obtained by reaction of U with N_2, must be interpreted in terms of high nitrogen activity a_N arising from high instability of flowing NH_3. At a given temperature the composition, i.e. the N:U ratio of α-U_2N_{3+x}, must be determined by the nitrogen activity a_N of the flowing gas phase consisting of NH_3, H_2 and N_2. When UC is reacted with NH_3 or N_2 at temperatures above 500 °C, α-U_2N_{3+x} and free carbon are formed. In this state an equilibrium between α-U_2N_{3+x} and the gas phase prevails and the free carbon does not take part in this equilibrium. Thus, even if UC is used as the starting material, the final state attained can be treated as an equilibrium between α-U_2N_{3+x} and the nitriding gas phase (flowing NH_3 or N_2). In this paper some problems associated with the reaction of U or UC with flowing NH_3 are discussed briefly. To examine these problems, some reaction experiments involving U+NH_3 (stream), UC+NH_3 (stream) and UC+N_2 (stream) have been performed at 600 and 900 °C.

2. Experimental details

2.1. Apparatus and materials

The experimental apparatus used in this work consists of a vacuum system, a gas supply system, a gas chromatograph system and a resistance furnace. The reaction tube made of quartz was fitted into the cylindrical resistance furnace. Ammonia gas (99.998%) was supplied from a commercial gas cylinder and was fed into the system through steel capillaries without further purification. UC was supplied by Mitsubishi Metal Mining Co. Ltd., Japan. Chemical analysis showed 95.00 wt.% U, 4.80 wt.% combined carbon and 0.03 wt.% free carbon. A metallic uranium ingot was supplied by Japan Power Reactor and Nuclear Development Corporation. The impurities of the uranium were given in a previous paper [8].

SSDI 0925-8388(94)04105-D

2.2. Procedure

About 0.3 g of a bright U chip was leached in 6 N HNO_3 for about 2 h and washed with water and 2-butyl alcohol. This U sample was converted by action of H_2 at 225 °C to powdered UH_3, which was then decomposed at 600 °C in vacuum to obtain powdered U. This process was repeated several times. A quartz boat containing the thus-pretreated U powder or UC sample was placed in the centre of the reaction tube and the system was evacuated to the order of 10^{-6} Pa at room temperature. After raising the temperature to 600 or 900 °C, NH_3 gas was constantly supplied into the reaction tube at a flow rate of 100 ml min^{-1} for a given reaction time. The extent of dissociation was determined by gas analysis of the outlet gas with a gas chromatograph (type GC-8BT, Shimadzu Co. Ltd., Kyoto, Japan). The X-ray diffraction patterns of the samples cooled quickly after the termination of runs were obtained with a diffractometer (Rigaku Denki; Geiger flex rad-rA). The N:U ratio of α-U_2N_{3+x} was determined from the lattice parameter values.

3. Results and discussion

First the following situation will be considered. NH_3 gas is supplied constantly at a given flow rate into a reaction tube, in the centre of which a powdered U specimen or UC sample is placed and kept at a high temperature. A certain degree of dissociation of NH_2 catalysed by the surfaces of the sample is unavoidable at high temperatures. The extent of dissociation, α, depends on the temperature, the flow rate of NH_3, the amount and surface properties of the sample and the diameter of the reaction tube. For example, when a reaction tube of larger diameter is used, a large amount of NH_3 does not participate in the reaction.

In reactions of U or UC with flowing NH_3 the nitridation reaction of U or UC, i.e. the α-U_2N_{3+x} formation reaction, may proceed in parallel with the catalytic decomposition of NH_3. Eventually a steady state may be established where P_{NH_3}, P_{H_2} and P_{N_2} in the flowing gas and the N:U ratio of α-U_2N_{3+x} are all uniquely determined. In this situation the gas phase itself is not in equilibrium, but a partial equilibrium between the gas phase and α-U_2N_{3+x} is established. In other words, of the two reactions, the decomposition of NH_3 and the formation of α-U_2N_{3+x}, the former is constrained to an unstable non-equilibrium state by flowing NH_3, but the nitridation may proceed at sufficient speed until the partial equilibrium is reached between the nitride and the gas phase, where the nitrogen activity a_N exhibited by the gas phase must be equal to that of the α-U_2N_{3+x} phase. The nitrogen activity a_N of the unstable gas phase of NH_3, H_2 and N_2 as prepared by flowing NH_3 is given by $a_N=(1/K_P)(P_{NH_3}/P_{H_2}{}^{3/2})$, where K_P is the equilibrium constant for $\frac{3}{2}H_2+\frac{1}{2}N_2=NH_3$ and the partial pressures are expressed in atmospheres [1]. Assuming that the total pressure of the flowing gas is 1 bar, a_N is expressed as a function of the extent of dissociation, α, as

$$a_N=\frac{1}{K_P}\frac{(1-\alpha)(1+\alpha)^2}{[3\alpha(1+\alpha)/2]^{3/2}} \qquad (1)$$

At a given temperature the N:U ratio of U_2N_{3+x} may become larger as the extent of dissociation, α, decreases, since the nitrogen activity a_N in the flowing gas increases with decreasing α.

The experimental results together with the experimental conditions are summarized in Table 1. Figures 1 and 2 show the variations in the total pressure (P_{total}) and the respective partial pressures of NH_3, H_2 and N_2 (P_{NH_3}, P_{H_2} and P_{N_2}) with time during the reaction of UC (0.3358 g) with NH_3 at 900 °C (run 3) and that of U powder (0.3194 g) with NH_3 at 900 °C (run 4) respectively. In the very early stage of runs P_{NH_3} drops and both P_{H_2} and P_{N_2} increase, then P_{NH_3} continues to decrease and P_{H_2} and P_{N_2} gradually increase. Eventually a stationary state is reached where P_{NH_3}, P_{H_2} and P_{N_2} all remains constant, at least within experimental error. The time dependences of P_{NH_3}, P_{H_2} and P_{N_2} are

TABLE 1. Experimental results

Run	Reaction	Reaction temperature (°C)	Reaction time (h)	$P_{NH_3}{}^a/P_{H_2}{}^{3/2}$	a_N	α	U_2N_{3+x}	
							Lattice parameter (nm)	N:U ratio
1	UC (1 g)+NH_3 (flow)	600	12	1.4155	957	0.473	1.0591	1.83
2	UC (2 g)+NH_3 (flow)	600	12	1.1247	761	0.518	1.0612	1.80
3	UC (0.3 g)+NH_3 (flow)	900	30	0.1109	503	0.877	1.0610	1.80
4	U (0.3 g)+NH_3 (flow)	900	20	0.0821	373	0.903	1.0617	1.79
5	UC (1 g)+N_2 (flow)	600	12	–	1	–	1.0649	1.69
6	UC (1 g)+N_2 (flow)	900	6	–	1	–	1.0659	1.65

[a] The units for P_{NH_3} and P_{H_2} are atmospheres, since the equilibrium constant K_P is used for calculations of the nitrogen activity a_N.

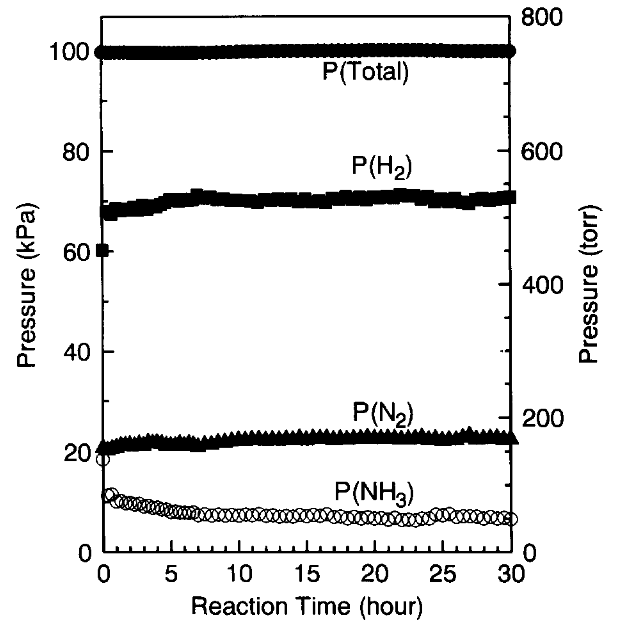

Fig. 1. Variations in P_{total}, P_{NH_3}, P_{H_2} and P_{N_2} with time during reaction of UC with NH_3 at 900 °C.

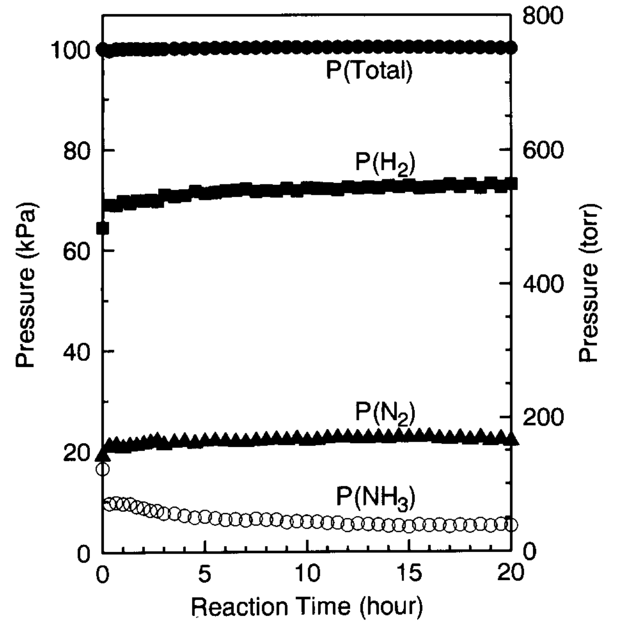

Fig. 2. Variations in P_{total}, P_{NH_3}, P_{H_2} and P_{N_2} with time during reaction of U powder with NH_3 at 900 °C.

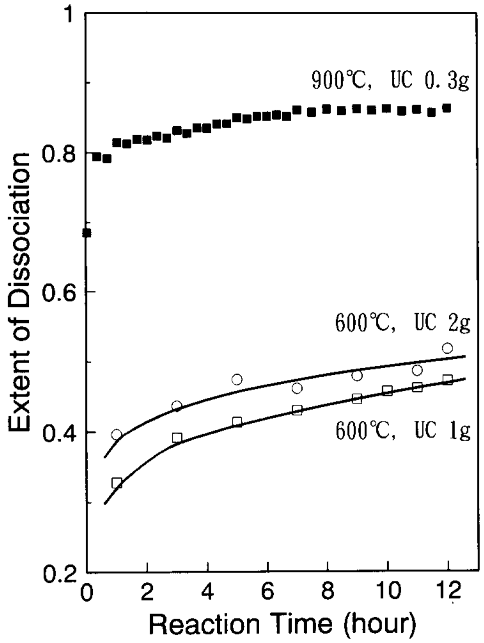

Fig. 3. Extent of dissociation of NH_3 into H_2 and N_2 as a function of reaction time.

essentially the same in runs 1 and 2. This may be due to the following two points: (i) the weight of UC and that of powdered U used as starting materials are almost the same; (ii) the same flow rate (100 ml min^{-1}) and the same temperature (900 °C) were chosen. The N:U ratio of α-U_2N_{3+x} obtained in run 3 is almost the same as that in run 4 and these two values are much larger than the N:U ratio of α-U_2N_{3+x} prepared by reaction of UC with N_2 at 1 bar ($a_N = 1$) at 900 °C (run 6) (see Table 1). The results for UC+NH_3 at 600 °C given in Table 1 clearly show the effect of the amount of UC used as starting material on the extent of dissociation, α. Although all the experimental conditions are the same in runs 1 and 2, except for the difference in the weights of UC samples used as starting material, a larger value was obtained for the extent of dissociation, α, in run 2 than in run 1, suggesting that the formation of α-U_2N_{3+x} acts as a catalyst for NH_3 decomposition and the amount of α-U_2N_{3+x} influences the value of α and hence the value of a_N. Although the reaction of UC with N_2 at 600 °C (run 5) results in the formation of α-U_2N_{3+x}, its N:U ratio is much smaller than those of α-U_2N_{3+x} obtained by reaction of UC with NH_3 (runs 1 and 2).

Figure 3 illustrates how α varies with the reaction time. The result obtained at 900 °C (run 3) shows that α rises sharply initially and continues to increase gradually until a stationary state is reached. In the case of reaction of UC with NH_3 α continues to increase. Stationary states will be reached even at 600 °C if the reaction time is extended.

4. Concluding remarks

Although it is possible to prepare α-U_2N_{3+x} by reactions of U or UC with N_2 at temperatures higher than 600 °C, the use of NH_3 instead of N_2 also leads to the formation of α-U_2N_{3+x} and the N:U ratio of the thus-prepared α-U_2N_{3+x} is much higher than that of α-U_2N_{3+x} prepared by U or UC+N_2 reaction. These results suggest that the nitrogen activity a_N is greatly enhanced by suppressing the dissociation of NH_3, which can be attained by flowing NH_3 through a high temperature region. The nitrogen activity a_N increases with decreasing extent of dissociation, α. The N:U ratio of α-U_2N_{3+x} in a partial equilibrium with a flowing gas become larger as the a_N value of the gas increases.

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