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OXIDATION BEHAVIOUR OF U_2N_3

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ABSTRACT

The kinetics of the oxidation of U_2N_3 containing 0.48, 16.2 and 21.1 mol% of UO_2 was studied by thermogravimetry under isothermal as well as non-isothermal heating conditions to identify the intermediate steps and the mechanism of reactions. Kinetic parameters such as apparent activation energy and pre-exponential factor were calculated for the proposed mechanism. The influence of the presence of UO_2 in the matrix on the mechanism of the process is discussed.

INTRODUCTION

Mixed uranium–plutonium nitrides constitute one of the advanced fuels for fast breeder reactors [1]. The nitride U_2N_3 is known to occur as an intermediate product during either the irradiation of UN or its reaction with oxygen [2]. A study of its oxidation behaviour was considered relevant, because conversion to oxide is one of the possible head-end steps for reprocessing nitride fuels. The presence of oxygen lowers the nitrogen potential, which is significant for decreasing the fuel–cladding interaction in nitride fuel [2]. Holleck and Ishii [3] have carried out DTA studies to obtain the decomposition temperatures of U_2N_3 in nitrogen atmospheres for samples containing 0.7 to 38 at.% of UO_2. In the present study, oxidation of U_2N_3 was carried out to investigate the mechanistic aspects while allowing UO_2 to be present in it as an impurity, since it was found to decrease the nitrogen pressure. The mechanism of the reaction was arrived at by treatment of the thermogravimetric data based on the calculations suggested by Doyle [4] and further modified by Zsako [5] for non-isothermal kinetic studies.

The basic expression for the integral methods of analysis of thermoanalytical curves as proposed by Doyle for non-isothermal studies is given by

$$g(\alpha) = ZEp(x)/qR \qquad (1)$$

where $g(\alpha)$ is a function of α, the fraction reacted, and $p(x)$ is a function of x defined as $x = E/RT$. Z, E, R, q and T are respectively the pre-exponential factor of the Arrhenius equation, the activation energy, the gas constant, the heating rate and the absolute temperature.

The fraction reacted is given as

$$\alpha = (W_0 - W_t)/(W_0 - W_f) \qquad (2)$$

where W_0, W_t and W_f are initial mass, mass at time t and final mass respectively. Zsako [5] and Skvara and Satava [6] used eqn. (1) in logarithmic form

$$\ln g(\alpha) - \ln p(x) = \ln ZE/qR \qquad (3)$$

As ln ZE/qR is constant for a given reaction at a constant heating rate, the plots of ln $g(\alpha)$ vs. T and ln $p(x)$ vs. T should be identical in shape [7], provided that the assumed mechanism for the calculation of $g(\alpha)$ and the activation energy for the calculation of $p(x)$ are correct. The values of functions $p(x)$ for a particular temperature and activation energy are reported by Zsako [5]. The standard deviation can be calculated for the values of the difference of ln $g(\alpha)$ and ln $p(x)$ for a particular assumed kinetic model in the temperature range of interest and for each assumed activation energy. The correct mechanism is that by which the standard deviation is minimum for a particular combination of activation energy and a kinetic model. Various kinetic models proposed by Bagchi and Sen [8] were used to fit the data from the present study.

In isothermal reaction, α values were obtained as a function of time at a particular temperature. The data were used to identify the correct mechanism by comparing the linearity of various plots of $g(\alpha)$ versus time using the least squares analysis technique. The forms of the $g(\alpha)$ equations are the same as those used in non-isothermal studies. The slope of the best linear plot is the reaction rate constant at that temperature. The temperature dependence of the rate constant yielded activation energy and pre-exponential factors.

EXPERIMENTAL

Preparation of U_2N_3

Samples of U_2N_3 in the form of microspheres were prepared by heating UO_3 gel particles, containing 2.35 to 2.5 mol of carbon per mol of uranium, in a stream of purified nitrogen (60 ml min^{-1} g^{-1}). The gel particles were prepared by the sol–gel process [9]. The microspheres sintered at 1973 K in N_2 had a specific surface area of 0.1 m^2 g^{-1}. X-ray diffraction and chemical analyses for oxygen were carried out on each sample before a run. The sesquinitrides so prepared did not contain carbon. The three samples used for the study had 0.03, 1.0 and 1.3% mass of oxygen, corresponding to the

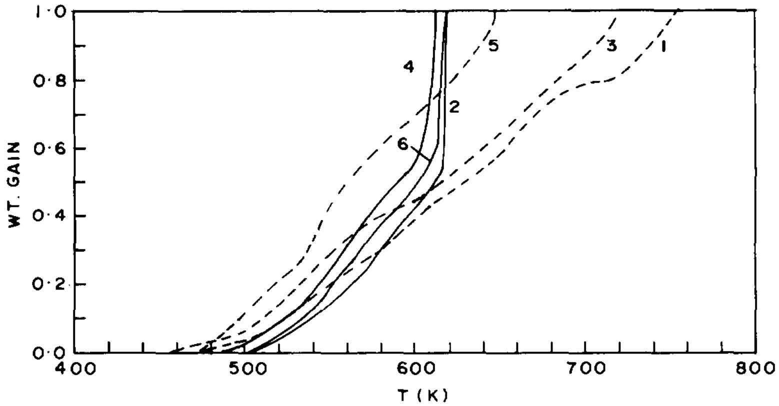

Fig. 1. Non-isothermal oxidation of U_2N_3 samples. Weight gain normalised to unity. p_{O_2}: — — —, 2×10^{-4} atm; ———, 0.21 atm. Curves 1 and 2 samples with 0.48 mol% UO_2; curves 3 and 4 samples with 16.2 mol% UO_2; curves 5 and 6 samples with 21.1 mol% UO_2.

presence of 0.48, 16.2 and 21.1 mol% of UO_2. About 30 mg of sample was taken in a platinum holder, which was found to be compatible with the samples in temperature range of the study. The sample was transferred to the holder in moisture-free carbon tetrachloride to prevent exposure to the atmosphere, and the holder was hung from one of the arms of an electrobalance. A quartz tube surrounded the sample holder and allowed the control of the reaction environment. The mass changes during heating were recorded by a Cahn vacuum electrobalance with a sensitivity of 10 μg/ and with direct registration of mass on the recorder. The sample was heated with a nichrome wire-wound furnace. A controlled heating rate of 4.5 K min^{-1} was maintained using an Indotherm programmer controller. The sample temperature was monitored independently by a calibrated chromel–alumel thermocouple placed 2 mm below the sample holder. Oxidation was carried out using argon containing 200 ppm of oxygen ($p_{O_2} = 2 \times 10^{-4}$ atm) and air ($p_{O_2} = 0.21$ atm). The thermograms recorded are given in Fig. 1; the mass gain in each experiment was normalised to unity corresponding to the formation of UO_2. The reaction products were analysed by the X-ray diffraction method.

RESULTS AND DISCUSSION

Non-isothermal kinetic studies

Thermogravimetric results on three types of sample under two oxygen environments are given in Fig. 1. The temperatures at which the conversion of U_2N_3 to UO_2 was initiated and detected by change in mass are given in Table 1. The mass gain following the oxidation was perceptible only above

TABLE 1

Conditions for oxidation of U_2N_3 samples under non-isothermal conditions

Oxygen partial pressure (atm)	Temperature of perceptible reaction (K) [a]	Completion temperature of reaction (K) [a]
U_2N_3 with 0.48 mol% UO_2		
2×10^{-4}	461	753
	467	755
0.21	503	614
	501	617
U_2N_3 with 16.2 mol% UO_2		
2×10^{-4}	452	720
	445	714
0.21	488	617
	478	621
U_2N_3 with 21.1 mol% UO_2		
2×10^{-4}	473	650
	478	652
0.21	503	638
	493	620

[a] Within ±2 K.

450 K in all cases, irrespective of oxygen pressure. The initiation temperature for oxidation of all U_2N_3 samples in air was higher than at lower oxygen partial pressure. This may be attributed to the high partial pressure of nitrogen in air, which may delay the reaction, although the large partial pressure of oxygen (0.21 atm) was expected to provide an instantaneous reaction on the nitride.

A computer program developed by Ravindran [10] was used for the analysis of the data. This analysis was carried out for each experiment at different oxygen partial pressures under non-isothermal heating conditions, taking all values of α from 0.3 to 0.9. The reaction mechanism seemed to be dominated by nucleation growth governed by the rate equation of the type $-\ln(1-\alpha)^r$, as suggested by Avrami [11]. The mechanism of nucleation growth for a reaction of the kind

$$U_2N_3(s) + O_2(g) \rightarrow UO_2(s) + N_2(g) \tag{4}$$

involving reacting and escaping gases appeared rare. The non-isothermal heating curves in Fig. 1 are far from the usual sigmoidal shape, thus making analysis of the data for the mechanism more complex. However, there seems to be more than one mechanism operating in the oxidation, as indicated by the nature of curves comprising various linear segments. Hence, the oxidation of U_2N_3 was studied under isothermal conditions also in order to establish the absence of diffusion control. For isothermal studies, diffusion appeared to be the primary rate controlling step.

Isothermal kinetic studies

The analysis of the data on the isothermal studies of each sample at different temperatures under an oxygen pressure of 2×10^{-4} atm are given in Table 2. Low oxygen pressure was used mainly to allow the reaction to proceed slowly so that intermediate phases could be identified. In a similar way to the non-isothermal studies, several kinetic models were tried in order to find out the best fit. The $g(\alpha)$ with time plots corresponding to a diffusion controlled mechanism were found to give the best fit.

The mechanism of nucleation growth could not be observed during isothermal studies, as this process might have already taken place by the time the sample attained the desired temperature.

The presence of UN as an intermediate phase was observed in samples containing UO_2 as a separate phase during the isothermal heating experiments. The samples were heated for 3 h at various temperatures at low oxygen pressure (2×10^{-4} atm). The product analysis by X-ray diffraction, as shown in Fig. 2, clearly indicated the presence of UN in the sample containing 21.1 mol% of UO_2 before the nitride was completely oxidised to UO_2. The sample with 16.2 mol% of UO_2 also indicated the UN phase, but to a lesser degree compared with the sample with 21.1 mol% of UO_2. No intermediate phase of UN could be identified with the sample containing 0.48 mol% of UO_2. The samples containing 0.48 mol% of UO_2 are within the

TABLE 2

Oxidation of various samples of U_2N_3 under isothermal conditions ($p_{O_2} = 2 \times 10^{-4}$ atm) [a]

Temp. (K)	Rate constant (log units)	$g(\alpha)$ (kinetic equation = kt)	E_a (kJ mol^{-1})	Z (s^{-1})
U_2N_3 with 0.48 mol% UO_2				
623	−12.4	$[(1+\alpha)^{1/3}-1]^2$	125	316
673	−12.1	$[(1+\alpha)^{1/3}-1]^2$		
723	−9.4	$[(1+\alpha)^{1/3}-1]^2$		
763	−9.0	$[(1+\alpha)^{1/3}-1]^2$		
U_2N_3 with 16.2 mol% UO_2				
581	−10.3	$[(1+\alpha)^{1/3}-1]^2$	59.8	1×10^4
603	−9.1	$[(1+\alpha)^{1/3}-1]^2$		
673	−8.1	$[(1+\alpha)^{1/3}-1]^2$		
723	−7.8	$[(1+\alpha)^{1/3}-1]^2$		
U_2N_3 with 21.1 mol% UO_2				
573	−8.9	α^2	52.3	4×10^3
603	−8.4	α^2		
673	−7.2	$[1-(1-\alpha)^{1/3}]^2$		
723	−6.7	$[1-(1-\alpha)^{1/3}]^2$		

[a] Mechanism is diffusion.

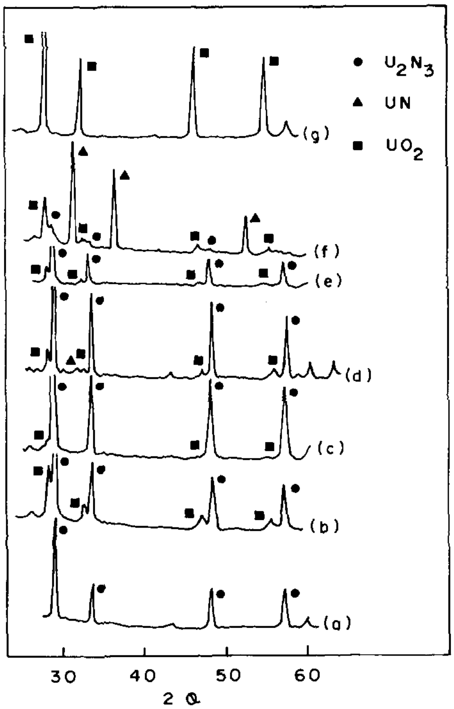

Fig. 2. X-ray-diffraction patterns of the intermediates during isothermal oxidation of U_2N_3: a, 373 K; b, 650 K U_2N_3 with 0.48 mol%UO_2; c, 373 K; d, 650 K U_2N_3 with 16.2 mol%UO_2; e, 373 K; f, 603 K U_2N_3 with 21.1 mol%UO_2; g, end product at 783 K.

solubility limit of UO_2 in U_2N_3 [12]. The solubility limit for UO_2 in U_2N_3 is reported to be ca. 5 at% at 1700 K. The samples containing 16.2 and 21.1 mol% of UO_2 are outside the limit of solubility, and hence their heating results in precipitation of the UO_2 phase. The UN intermediate could be observed only with a U_2N_3 sample containing substantial amounts of UO_2 as a separate phase. This observation could be attributed to one of the following reasons.

(a) The presence of UO_2 dispersed homogeneously brings down the decomposition temperature of U_2N_3 from 700 °C, as reported by Bugl and Bauer [13] and by Dell et al. [14], to the present temperature of study.

$$U_2N_3 \rightarrow 2UN + \tfrac{1}{2}N_2(g) \qquad (5)$$

From the data available on the Gibbs free energy of formation for UN and U_2N_3 [15] the equilibrium partial pressure of nitrogen for reaction (5) at 600 K is only 3.8×10^{-17} atm. This rules out reaction (5) as a route of UN formation in oxidation of U_2N_3.

(b) The formation of UN as an intermediate phase could possibly take place by the reaction

$$U_2N_3 + xO_2 \rightarrow xUO_2 + (2 - x)UN + (1 + x)/2N_2 \qquad (6)$$

The equilibrium nitrogen partial pressure of this reaction at 600 K for p_{O_2} of 2×10^{-4} atm is 9.8×10^{51} atm for $x = 1$.

General discussion

Holleck and Ishii [3] have carried out DTA measurements on U_2N_3 in a nitrogen atmosphere to determine the transition and decomposition temperatures with and without oxygen impurity in the gas phase. They observed that transition and decomposition temperatures of U_2N_3 increase when oxygen is present in static nitrogen atmospheres. They report oxidation of U_2N_3 at temperatures above 1273 K and in the presence of nitrogen having more than 10% vol. of oxygen. In the present study, oxidation of U_2N_3 was observed above 450 K and in an atmosphere having p_{O_2} of 2×10^{-4} atm. Holleck and Ishii have also studied the effect of UO_2 on the decomposition of U_2N_3. They report that, when UO_2 is present in the dissolved state, the decomposition goes through an oxynitride intermediate, whereas, when UO_2 is present as a separate phase, the decomposition proceeds to UN without an oxynitride phase.

$$[U_2N_3(\alpha \text{ phase}) + UO_2] \rightarrow UN + UO_2 + N_2 \tag{7}$$

The decomposition of U_2N_3 by reaction (5) should be accompanied by a mass loss, but the reaction proceeds with a mass gain. Hence there may be one or more competitive reactions to yield UN as an intermediate phase with a mass gain as observed.

The presence of UN as an intermediate phase, as shown by XRD on samples containing UO_2 as a separate phase, indicates the important role played by the homogeneous distribution of UO_2 in the entire U_2N_3 matrix. The absence of UN in other samples when a substantial amount of UO_2 formed during the oxidation reaction is present only at the reaction front lends further support to the observation that UN is formed only in U_2N_3 samples containing UO_2 as a separate homogeneously dispersed phase.

The fitting of complete non-isothermal data of each experiment to a single reaction mechanism indicated nucleation growth as the primary rate controlling mechanism, even though diffusion was expected to play a role when gaseous species are present in the reactant as well as the product side. This can be attributed to the process of data treatment, in which the process with the lowest standard deviation value among the various processes dominates as the rate controlling process for the overall reaction. Therefore, simple interpretation of statistical data would suggest a nucleation growth process as the rate controlling step although diffusion also occurs as rate control in the latter course of the reaction. Since the numerical range of $g(\alpha)$ for the Avrami–Erofeyev equation is much smaller than for other models, the curvature of the plots would always be less [16].

CONCLUSION

The conclusions arrived at from the present investigation are as follows.

(i) During the oxidation of U_2N_3, more than one mechanism was observed to operate during the entire course of reaction.

(ii) Disagreement in mechanism was observed for non-isothermal and isothermal heating modes when all values of α ranging from 0.3 to 0.9 were considered.

(iii) UN is formed as an intermediate from U_2N_3 under low oxygen pressure when UO_2 is present as a separate phase.

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