

The oxidation of uranium diboride in flowing air atmospheres

Mistarihi, Q; Martini, Fabio; Buckley, J; Middleburgh, Simon; Abram, Tim; Turner, Joel

Journal of Nuclear Materials

DOI: https://doi.org/10.1016/j.jnucmat.2023.154417

Published: 01/07/2023

Publisher's PDF, also known as Version of record

Cyswllt i'r cyhoeddiad / Link to publication

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA): Mistarihi, Q., Martini, F., Buckley, J., Middleburgh, S., Abram, T., & Turner, J. (2023). The oxidation of uranium diboride in flowing air atmospheres. *Journal of Nuclear Materials*, Article 154417. https://doi.org/10.1016/j.jnucmat.2023.154417

Hawliau Cyffredinol / General rights Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

· Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
 You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Contents lists available at ScienceDirect



Journal of Nuclear Materials



journal homepage: www.elsevier.com/locate/jnucmat

The oxidation of uranium diboride in flowing air atmospheres

Q. Mistarihi^a, F. Martini^b, J. Buckley^a, S.C. Middleburgh^b, T.J. Abram^a, J. Turner^{a,*}

 $^{\rm a}$ The University of Manchester, Oxford Road, Manchester, United Kingdom $^{\rm b}$ Bangor University, Bangor, United Kingdom

ARTICLE INFO

Article history: Received 13 January 2023 Revised 27 March 2023 Accepted 28 March 2023 Available online 1 April 2023

Keywords: Nuclear fuel Oxidation Uranium

ABSTRACT

The air oxidation behaviour of UB₂ synthesized via the carbo/borothermic reaction has been investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), through heating ramp and isothermal studies. Heating ramps from room temperature up to 1173 K showed an on-set of rapid oxidation occurred at a temperature of 807 ± 6 K for samples in fragment form and 799 ± 5 K for finely powdered material. The ramp tests yielded UB₂O₆ as the ultimate oxidation product. A thermodynamic model for the U-B-O system was used to propose a reaction pathway for the oxidation process in excess oxidiser condition and to predict the amount of heat released. The predictions of the model agreed with the observed phenomena and with the values measured via DSC.

© 2023 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/)

1. Introduction

Uranium diboride (UB₂) has many attractive properties that make it a good candidate for application as a nuclear fuel material. It has a high thermal conductivity ($\sim 24 \text{ W/m} \cdot \text{K}$ at 1273 K) [1] which is higher than UO_2 (~ 2.8 W/m·K) and other candidate fuels materials such as uranium mononitride (UN, 21 W/m·K) and uranium sesquisilicide (U₃Si₂, 19 W/m·K) [2]. Its uranium density (11.68 g/cm^3) is higher than that of UO₂ (9.75 g/cm³), and comparable to those of UN (12.9 g/cm³) and U_3Si_2 (12.2 g/cm³) [3]. A higher thermal conductivity can reduce fuel centreline temperatures, and therefore lead to reduced fission gas release and pelletcladding mechanical interaction in-service [4]. Having a high uranium density is beneficial for fuel economy, as it can allow for increased fuel cycle length and/or fuel burn-up [5]. Despite these attractive properties, its application is limited by the high thermal neutron absorption cross-section of the boron-10 isotope. In addition, the fabrication process of UB₂ via conventional techniques is difficult and requires sintering at high temperatures for an extended time (~ 2373 K for 4 h to achieve 93% relative density) owing to its high melting point and the suspected formation of an oxide layer on the surface of the starting powder, even in low oxygen conditions [6,25]. The use of non-conventional sintering techniques like spark plasma sintering or the use of carbon to eliminate the existence of surface oxide layers has been found to be effective in enhancing the densification of UB₂ [1,7]. Enrichment

* Corresponding author. E-mail address: joel.turner@manchester.ac.uk (J. Turner). of boron with the boron-11 isotope, which has a much lower thermal neutron absorption cross-section can potentially provide a solution for the high neutron absorption cross-section of UB₂. Boron enrichment is an established technology, although not on the scale required for fuel pellet manufacture. Natural boron is only ~20% boron-10, while high-purity boron-10 is needed for use in control rods, requiring significant enrichment and producing boron-11 as a by-product.

Recently, there has been a renewed interest in using UB₂ as an advanced technology fuel (ATF) material. The addition of UB2 has been found to improve the oxidation resistance of other candidate accident tolerant fuel materials in several studies. For example, Turner et al. [8] demonstrated U₃Si₂-UB₂ composites which showed improved oxidation resistance in a steam environment, increasing the onset temperature by \sim 170 K with 10 wt.% of UB₂. An increase in the onset oxidation temperature by 120 K was also observed when 5 wt.% of UB_2 was added to UN and oxidized in a steam environment up to 1173 K [9]. UB₂ has a higher steam oxidation resistance than both UN and U₃Si₂ with an onset oxidation temperature of 902 K [8,9]. However, a detailed study on the oxidation behaviour of UB₂ in steam has not yet been conducted. Although steam environments are generally of most interest for light water reactor applications, air oxidation studies can provide useful information such as oxidation mechanisms and kinetics of the reaction.

In the present study, the oxidation behaviour in air of UB_2 synthesized via the carbo/borthermic reduction reaction is investigated. Experimental studies including oxidation ramps up to 1173 K and oxidation isotherms in the temperature range of 773–1023 K were performed to investigate the oxidation mechanism

https://doi.org/10.1016/j.jnucmat.2023.154417

0022-3115/© 2023 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/)



Fig. 1. Size and morphology of UB₂ samples used for oxidation testing. A: Fragment samples. B: Fine powder samples.

and kinetics of UB_2 in an air atmosphere. The oxidized powder was characterized using thermogravimetry-differential scanning calorimetry (TG-DSC) and X-ray diffractometry (XRD). In addition, a computational thermodynamic study was performed to calculate the Gibbs free energy change for the possible reactions that may occur during the oxidation of UB_2 in an air atmosphere.

2. Methodology

2.1. Sample preparation

UB₂ powder samples were prepared by the carbo/borthermic reduction synthesis route as reported in Ref. [10]. UO₂₀₂ (ABSCO LTD, UK), B₄C (Sigma Aldrich, 99.7%), and powdered nuclear grade graphite (NBG-18) were mixed with a molar ratio of 1.86:3.04:1.00 for 4 h in a planetary ball mill (Retsch PBM 200) at a milling speed of 400 rpm and using tungsten carbide vessels and milling media. Mixed powder was pressed into a green pellet using a uniaxial press and the green pellet heated to 2073 K for 30 min in a vacuum atmosphere. The synthesised UB₂ was crushed into fragments or further ground into fine powder (Fig. 1A and B respectively) using a mortar and pestle. Fragment samples had an average particle size of around 400 µm, with a small proportion of finer material which broke from the relatively poorly sintered larger pieces. Fine powder consisted of much smaller particles, with an average size of around 31 µm. Microscopy of initial material showed small, likely closed porosity on the surface of both fragment and fine powder material. This is not unexpected as the synthesis method used evolves CO as a product alongside UB₂. Material was not milled and re-sintered as this may introduce additional impurity compounds throughout the final pellet.

The crystal structure of the synthesized UB₂ was investigated using XRD (Malvern Panalytical Empyrean) using CuK α radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 40 mA. Material purity was determined by the Rietveld method and found to be $94 \pm 1\%$ pure by mass, with the balance being UO₂ as the only other detectable crystalline phase, as shown in Fig. 2. This phase is expected to be distributed throughout the material rather a result of uniform surface oxidation. XRD penetration is only around 5 µm for uranic materials and so the development of 6% UO₂ on the powder surface would prevent the detection of the underlying UB₂. Similar levels of impurity have been detected following UB₂ synthesis in related work [10] and this was therefore in line with expectations.

Light element impurity content was determined through combustion analysis with a Thermo ScientificTM FLASH 2000 Analyser, and the material was found to contain 0.1 wt% residual carbon following synthesis.

2.2. Oxidation experiments

Heating ramps and isothermal testing were performed in synthetic air to study the oxidation behaviour of UB₂. Approximately 20–25 mg of UB₂ material was used in each test, either in powder or fragment form. The specific form tested is noted within the relevant text and figure throughout.

For heating ramps, fine powders and fragments were heated in a synthetic air atmosphere (BOC-certified 21.49% O_2 in N_2) up to 1173 K with a heating rate of 1–10 K/min. TG-DSC was performed using a Netzsch STA449 F1 simultaneous thermal analyser to study the oxidation behaviour of UB₂ during ramp testing.

Thermogravimetric analysis (TGA) was used to observe the oxidation behaviour of UB₂ during isothermal testing. UB₂ powder was heated to the desired temperature (773–1123 K) in a flowing Ar (99.99%, 130 mL/min) with a heating rate of 10 °C/min. Once the target temperature was reached, the sample was held at temperature for 10 min before the gas was switched from Ar to synthetic air flowing at a rate of 100 mL/min. The sample was held at the target temperature for 1–3 h and then cooled in flowing Ar



Fig. 2. XRD of as-synthesised UB₂ powder.

(130 mL/min) to room temperature. The crystal structure of the oxidation products was analysed using XRD as above.

3. Thermodynamic modelling

A thermodynamic model was developed to calculate the change in enthalpy, entropy, and Gibbs free energy as a function of temperature for various relevant reactions in the U-B-O system, using the thermodynamic data reported in the literature for B_2O_3 , O_2 , UB_2 , UB_4 , UB_{12} , UO_2 , U_3O_8 , and UB_2O_6 [11–16]. The more negative the variation in Gibbs free energy, the more thermodynamically preferred a given process will be.

The order of preference reflects the quasi-equilibrium pathway of the overall process of oxidation of UB_2 . The quasi-equilibrium pathway, represents the case in which one or more of the reactants are added in infinitesimal increments and the system is allowed to reach chemical and thermal equilibrium after each addition. While notably idealised – no kinetic or diffusion limitations are considered – such a model may still help in predicting which reaction may be the most likely to occur amongst the available chemical species.

Figure 3a and b show the order of preference of several possible oxidation reactions when uranium compounds and oxygen are the limiting reactants, respectively. This distinction is achieved by referring the variation in Gibbs free energy associated with each reaction to the amounts of uranium or oxygen involved, respectively, so that the limiting reactant is allocated where it minimises the Gibbs free energy of the products most effectively. It is also worth noting that the order of preference described in Fig. 3b is independent of the chemical potential of oxygen, since a higher or lower chemical potential of O_2 would uniformly shift all the lines in the plots downwards or upwards, respectively. The order of preference is therefore conserved for any partial pressures of O_2 and for any oxidisers, including water and other oxygen-bearing substances.

In the oxidation experiments performed in this work approximately 0.1 mmol UB₂ is exposed to approximately 1 mmol O_2 per minute over the course of several hours, indicating that the process may be best modelled as occurring in oxygen-rich conditions.

Figure 3a shows that the thermodynamically preferred way to combine UB_2 and O_2 in oxygen-rich conditions is via reaction 1 proceeding to completion, followed by the oxidation of the pro-

duced UO₂ to U₃O₈ via reaction 2. The early stages of the oxidation would necessarily entail the formation of hyperstoichiometric uranium dioxide UO_{2+x}, since UO₂ would be the sole acceptor for oxygen at this point of the pathway [17]. A further oxidation of U₃O₈ and its combination with B₂O₃ result in the formation of UB₂O₆ (reaction 3).

$$2 UB_2 + 5O_2 \to UO_2 + 2B_2O_3 \tag{1}$$

$$3UO_2 + O_2 \rightarrow U_3O_8 \tag{2}$$

$$2U_3O_8 + O_2 + 6B_2O_3 \to 6UB_2O_6 \tag{3}$$

It is worth noting that reaction 1 is favourable enough to drive reaction 2 backwards in both oxygen-rich and oxygen-poor conditions, indicating that UO_{2+x} and U_3O_8 may act as oxidisers when in contact with UB_2 . The oxidation would then occur at the interface until the local chemical potential of oxygen is low enough that the reaction stops or until enough reaction products (B_2O_3 in particular) accumulate forming another barrier layer. This may be relevant when such compounds form barriers between UB_2 and the surrounding oxidising environment, since the oxidation of the underlying UB_2 would be thermodynamically favoured and only kinetically limited by the transport of oxygen and boron oxide across the oxide layer.

In oxygen-poor conditions (Fig. 3b), as oxygen is added, the most thermodynamically stable composition is initially obtained by the formal disproportionation of the uranium borides, with U being oxidised to UO_2 and B accumulating into increasingly boronrich phases such as UB_4 and UB_{12} (Reactions 4 and 5). As more oxygen is added the higher borides are oxidised to UO_2 and B_2O_3 (Reactions 6 and 7), which would then react according to reactions 2 and 3.

$$2UB_2 + O_2 \rightarrow UB_4 + UO_2 \tag{4}$$

$$3UB_4 + O_2 \rightarrow UB_{12} + UO_2 \tag{5}$$

$$UB_4 + 4O_2 \to UO_2 + 2B_2O_3 \tag{6}$$



Fig. 3. The variation in Gibbs free energy for relevant reactions in the oxidation of UB₂. Free energies are calculated at an oxygen partial pressure of 0.2 bar and are referred to the reaction of 1 mol of U (a) and to 1 mol of O₂ (b), representing conditions in which uranium compounds and oxygen are the limiting reactants, respectively.

$$UB_{12} + 10O_2 \to UO_2 + 6B_2O_3 \tag{7}$$

The model can be validated against the available experimental data regarding the U-B-O system. For oxygen-rich conditions, the oxidation of UB₄ in flowing air as described by Guo et al. appears to follow the quasi-equilibrium pathway predicted by Fig. 3a, with the process occurring through reactions 6, 2, and, 3 [18]. Guo et al. also observed the reversal of reaction 3, with the decomposition of UB₂O₆, in the range 1273–1473 K, in agreement with the results of Hoekstra et al. (1373 K) [19] and the prediction of the model (1355 K). For oxygen-poor conditions, Kardoulaki et al. observed the formation of UB₄ and UO₂ in roughly equal amounts at the UB₂-UO₂ interface in solid samples of a UB₂-UO₂ composite heated under an inert atmosphere, with UO₂ acting as an oxidiser. In fact, reaction 4 is so thermodynamically favourable that it can strip oxygen from hyperstoichiometric and even hypostoichiometric UO₂ at temperatures as low as 700 K, according to the data on equilibrium partial pressures of oxygen of UO_{2+x} reported by Blackburn [20]. While this provides experimental evidence of reaction 4 occurring, no UB₁₂ was observed to provide evidence for the occurrence of reaction 5 [21]. However, it must be noted that the majority of the sample was still constituted of UB₂, in the presence of which UB₁₂ owing to reaction 8:

$$UB_{12} + 4UB_2 \rightarrow 5UB_4 \tag{8}$$

No UB_{12} was detected in an analogous UB_4 - UO_2 composite, but an anomaly in the thermal diffusivity suggested the formation of a new phase which could not be detected by XRD, likely because of low crystallinity [21]. The lack of conclusive evidence on the formation of UB_{12} may be due to it forming but having low crystallinity (and thus not being easily detectable), or to it not forming in appreciable amounts due to a low reaction rate – likely heavily limited by diffusion considering the significant amounts of boron that would require to be relocated to obtain UB_{12} from UB_4 .

The heat produced by the oxidation reactions was calculated from the thermodynamic model and complemented with the data provided by TGA. Since the oxidation reaction occurs over a range of temperatures and the enthalpy of reaction depends on temperature, the total heat released by the oxidation process Q_{OX} was calculated as

$$Q_{OX} = \int_{0}^{1} \Delta_{R} H(T(X)) \cdot dX$$

Where $\Delta_R H(T(X))$ is the enthalpy of reaction as a function of temperature *T* and *X* is the extent of reaction as measured by TGA, ranging between 0 (no reaction has occurred) and 1 (reaction complete, i.e. the maximum mass change has been achieved).

4. Results

4.1. Ramp testing

The mass change observed during the oxidation of UB₂ powder and fragments with increasing temperature up to 1173 K in flowing synthetic air and with a ramp rate of 3 K/min is shown in Fig. 4. The onset of the oxidation reaction (defined as the temperature at which 5% of the total mass increase observed was reached, shown in the inset in Fig. 3) was 807 \pm 6 K for samples in fragment form and 799 \pm 5 K for samples in fine powder form. The total mass gain on samples shown in Fig. 3 was 35.2 \pm 0.4% and 35.1 \pm 0.6% for fragments and fine powder respectively.

XRD patterns of the mixture of oxidation products revealed uranium borate (UB_2O_6) as the sole crystalline component (Fig. 5), which is compatible with the thermodynamic model. The theoretical mass gain due to the oxidation of UB_2 to UB_2O_6 amounts to 37.0% of the initial mass, which is very close to what was experimentally measured by TGA during the process, particularly if initial UO_2 impurities are also considered.

DSC measurements obtained during the oxidation of UB₂ fragments and powder are shown in Fig. 6. The oxidation of fragments produced two sharp DSC peaks at approximately 845 K and 921 K, while the oxidation of UB₂ powder appeared to be more uniform, presenting two blunter, overlapping peaks at temperatures of 849 K and 905 K. The total energy released during the oxidation of UB₂ fragments and powder, as calculated from the integration of the DSC curves, was 8.4 ± 0.1 J/mg and 8.2 ± 0.1 J/mg, respectively.

The expected value for the total heat produced by the oxidation reaction was calculated by considering the overall process of oxidation of UB_2 to UB_2O_6 , as the latter was the sole crystalline material identified amongst the products.

$$UB_2 + 3O_2 \rightarrow UB_2O_6 \tag{9}$$

Over three replicated runs, fine powders of UB₂ show a mass increase of 34.5 \pm 0.6%, while larger fragments show a mass increase of 35.5 \pm 0.5%. The heat released by oxidation was mea-



Fig. 4. Mass gain during the air oxidation of UB₂ fine powder and fragments. Inset shows oxidation onset temperatures determined from 5% of the final mass gain.



Fig. 5. XRD patterns for UB₂ oxidation product.

sured by DSC to be 8.2 \pm 0.1 J/mg and 8.4 \pm 0.1 J/mg, respectively (referred to the initial sample mass) as predicted by the thermodynamic model and by atomic masses a pure UB₂ sample being completely oxidised to UB₂O₆ would release 9.1 J/mg of heat and would register a 37.0% mass increase. However, considering the initial amount of UO₂ contained as an impurity in the samples (6 \pm 1% by mass), which can be assumed to be oxidised to U₃O₈, the predicted values for mass increase and the heat released are reduced to 34.8 \pm 0.4% and 8.5 \pm 0.1 J/mg. The values of the mass gain and of the heat released in the oxidation of both fine powders and fragments are therefore in good agreement with the values predicted by the thermodynamic model for the formation of a mixture of U₃O₈, and UB₂O₆.

Experiments with varying heating rates were performed to discern more effectively the stages of the reaction (Fig. 7). At low ramping rates, processes occurring at different times may instead occur at similar temperature values and thus be observed with an insufficient resolution. Up to three stages could be observed with a heating rate of 10 K/min.

4.2. Isothermal testing

Isothermal oxidation experiments were conducted to study reaction kinetics. The mass gain during the isothermal oxidation of UB₂ powder between 773 and 1023 K is shown in Fig. 8, which shows both a variation in reaction rate but also in the form of the mass gain curve between predominantly linear behaviour at low temperature to more complex forms above 848 K.

The diffraction patterns of the products of the UB_2 oxidation isotherms are shown in Fig. 9. In addition to UB_2 , both UO_2 and



Fig. 6. DSC profiles during the oxidation of UB₂ fragments and fine powder up to 1173 K.



Fig. 7. Mass gain during the oxidation of UB₂ fragments in air at different heating rates.

 U_3O_8 were detected in the samples oxidized at 773 K. With the increase in the oxidation temperature from 773 K to 823 K, the intensity of UO_2 and UB_2 diffraction peaks decreases and U_3O_8 becomes the prevalent phase. UB₂ diffraction peaks are no longer visible following oxidation at 848 K, and the remaining oxidation products are mostly composed of UO_2 and U_3O_8 . At 923 K, the diffraction peaks of UO_2 disappeared and UB_2O_6 diffraction peaks started to appear.

At °C 923–1023 K, no diffraction peaks of UO_2 were observed, and the oxidation products were composed of UB_2O_6 and U_3O_8 . Where UB_2 is still present in Fig. 9 this is likely a result of unreacted of material, which agrees well with the mass gains shown in Fig. 8. No peak shifts were observed within the phases identified in Fig. 9, suggesting for example that the oxygen is not absorbed within the UB_2 lattice in significant amounts prior to the formation of oxide phases.

4.3. Partial oxidation

Fragments of UB_2 were heated to 923 K in flowing air and then cooled under inert atmosphere in order to observe microstructural changes to the material. XRD was also attempted on these samples but gave inconclusive results due to the fragment morphology and low X-ray penetration. Fragments were resin mounted and polished to produce a cross section, which is shown in Fig. 10. Quantitative EDS on material containing boron, uranium and potentially



Fig. 8. Mass gain as a function of time during the oxidation isotherms of UB₂ powder at different temperatures.



Fig. 9. XRD of the oxidation isotherms products at different temperatures.

carbon is challenging due to a significant peak overlap between the X-rays emitted by three elements when using the technique, as well as the assumptions required to quantify EDS spectra within a material which is itself highly-absorbing to X-rays. Fig. 10 therefore provides a qualitative insight into the arrangement of phases within the material and allows for the identification of oxygen or boron-rich regions and phases, rather than a direct measurement of their composition. As can be seen from Fig. 10, three distinct phases were identified via EDS. The original UB₂ remains visible throughout the microstructure after the short oxidation exposure. A large amount of porosity was identified which formed as a result of the UB₂ synthesis method employed and was also visible on non-exposed fragments (Fig. 1). At the edge of some pores it is possible to identify a layer of material containing uranium, oxygen and possibly boron, and which may be UB₂O₆ or UO₂. This phase appears to be



Fig. 10. EDS and electron micrograph of UB2 heated to 923 K in flowing air and then cooled under inert atmosphere.





poorly crystalline compared to the bulk UB_2 material, although the absence of polishing artefacts within the phase suggest that this may be material below the polished surface which has become exposed as a result of pull-out during sample preparation. A boron rich phase was also identified within some pores which appears to contain some oxygen but not uranium. It is probable that these are B_2O_3 which supports the thermodynamic model in the absence of the observation of crystalline B_2O_3 via XRD.

5. Discussion

Fine powder samples exhibited systematically lower mass gain and heat released than the fragments tested, although the differences were small and within the bounds of the measurement uncertainty. This phenomenon may be due to a partial oxidation of the samples at room temperature prior to the experiment, resulting from their greater surface area. This interpretation is supported by the fact that the ratio of heat released per relative mass gain is equal within experimental precision across the two sample groups (0.232 \pm 0.006 J/(mg·%) and 0.229 \pm 0.006 J/(mg·%), respectively, indicating that the mass gain and the heat released are correlated to the amount of unoxidized UB_2 in the samples. Alternatively, again due to their greater surface area of the fine powder samples, loss of volatile B_2O_3 via evaporation may be enhanced during their oxidation, leading to a smaller net mass gain being observed and to part of the heat produced by the oxidation being used to drive the endothermic evaporation of B_2O_3 [22]. Within work studying the steam reaction with UB₂ a significant mass loss was observed above 1173 K, which was ascribed to this phenomenon, but no mass loss was seen in the present work, suggesting the former description may more readily explain the data [8].

For both the fragment and the fine powder samples the two peaks in DSC are matched in position by peaks in the 1st derivative of the mass profile (see Fig. 11). The ratio between the 1st derivative of the TGA signal and the magnitude of the DSC signal slightly increases with temperature. This is compatible with the decreasing trend in heat released per mass gain across reactions 1, 2, and 3, suggesting the increasing prevalence of reactions 2 and 3 in the process at higher temperatures.



Fig. 11. Fitting of the UB2 oxidation isotherms data at different temperatures: (a) 773 K, (b) 798 K, (c) 823 K, (d) 848 K, (e) 873 K (f) 923 K.

The stepwise oxidation behaviour shown with varying ramp rates (Fig. 7) suggests a mechanism based on the formation of a protective layer of B_2O_3 and UO_2 and its subsequent disruption, leading to the exposure of the fresh underlying material. As described previously, at higher temperatures, UO_2 is also oxidised to U_3O_8 and U_3O_8 combines with B_2O_3 to yield UB_2O_6 .

From isothermal testing the kinetics of UB_2 oxidation appear to be complex, and fitting with simple linear, parabolic, or logarithmic laws proved unsatisfactory. A multiple law model developed by Nickel et al. [23], containing both linear and parabolic contributions, was used to fit the isothermal oxidation data in the range 773–873 K (Fig. 11). The mass gain as a function of time can be

Table 1

Reaction rate constants from the analysis of the initial linear section of the mass gain profile for the isothermal data in Fig. 5.

Oxidation temperature (K)	$K_{lin} (mg \cdot mg^{-1} \cdot s^{-1})$	$K_{par}~(mg{\cdot}mg^{-1}{\cdot}s^{-1})$	R ²
773	0.0203	0.3165	0.9997
798	0.0144	1.5344	0.9996
823	-0.0337	1.9620	0.9996
848	-0.0775	3.5404	0.9975
873	-1.3948	19.0661	0.9770



Fig. 12. Arrhenius plot of reaction rate data from air oxidation of UB_2 powders.

Ea

expressed according to the following equation:

$$w = A + K_{\rm lin}t + K_{\rm par}\sqrt{t} \tag{10}$$

Where w is the mass as a function of time, A is a constant, K_{lin} is the linear constant, K_{par} is the parabolic constant, t is time. At 873 K and above, however, fitting of the mass gain profile with the multiple law model produced a poor fit and a logistic model was found to provide a better description of the phenomena. The K parameters and R^2 values corresponding to fitting are given in Table 1.

As can be seen from Fig. 11 and Table 1, UB₂ oxidation has a linear-parabolic form in the temperature range of 773–873 K with the parabolic term dominating, and increasing with the increasing temperature, suggesting the formation of an oxide layer which is volatile to some extent, typically associated with a negative linear kinetic term [24]. The linear term is positive at 773 and 798 K, which is related to the mass gain due to the chemical interaction between UB₂ and O₂. B₂O₃ phases have melting points consistent with the transition to a negative linear kinetic term shown in Table 1 (>823 K), and therefore the observed behaviour may be explained by the formation of a mixed UO₂ and B₂O₃ layer, which is disrupted above 823 K as the B₂O₃ forms a liquid phase. Alternatively the presence of U₃O₈ is much more significant at these

temperatures (Fig. 9) and this may play a role in the change in behaviour – disrupting the layer as it forms. Further work is required to better understand the role U_3O_8 and B_2O_3 play at these temperatures.

The reaction rate constant can be represented in the Arrhenius formula (Equation 1).

$$K_i = A e^{-\frac{\pi}{R}T} \tag{11}$$

Where A is the pre-exponential factor, E_a is the activation energy in J·mol⁻¹, R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), and T is the temperature in K. By plotting the logarithm of the reaction rate against 1000/T (Fig. 12), the activation energy at each temperature can be determined from the slope of the curve at that point.

The activation energy for the parabolic contribution, being the most dominant process during the oxidation of UB_2 in the temperature range of 773–873 K, was plotted but found to produce a poor linear fit, likely due to the competing contributions from both linear and parabolic relationships which also vary with temperature. The reaction kinetics were found to follow two distinct regimes, as distinguished by temperature. The value of the apparent activation energy E_a was calculated to be 380 kJ/mol below 873 K and 25 kJ/mol above 873 K. Note that these values of E_a are apparent since they refer to the overall oxidation process, in turn resulting from the combination of several elementary reaction steps for which the activation energies cannot be measured individually.

The behaviour of E_a is consistent with the discussion of reaction kinetics above, and suggests that a protective layer composed of glassy B_2O_3 and crystalline UO_2 and U_3O_8 forms at the UB_2 surface in the initial stages of the oxidation. The diffusion of oxygen across said layer may represent the rate-limiting step in the oxidation of the underlying UB_2 , leading to a slow rate of reaction at relatively low temperatures. Upon increasing the temperature above the threshold of 873 K this layer becomes more permeable to oxygen, either as the boron oxide phase is disrupted or through the formation of higher uranium oxides, leading to a significant reduction in the energy barrier for the oxidation process.

At temperatures below 1373-1473 K the oxidation of metal borides usually results in the formation of the corresponding metal oxides and a separate, glassy B2O3 phase, which usually has a protective effect on the underlying material [25]. Above 1473 K, the protective B₂O₃ layer evaporates due to its relatively high vapour pressure. For certain borides such as AlB₂ [26] and MgB₂ [27] the metal oxide and the boron oxide combine, leading to the formation of aluminium borate (Al₄B₂O₉) and magnesium borate (Mg₂B₂O₃, Mg₂B₂O₅), decomposing back into their respective oxides at high temperatures. UB₂O₆ has been observed in literature to form through the reaction between U_3O_8 and B_2O_3 in air at temperatures below 1373 K [28]. Therefore, the oxidation of UB₂ is likely to progress via the formation of UO₂ and B₂O₃ (see reaction 1), followed by the oxidation of UO_2 into U_3O_8 (see reaction 2), and finally the formation of UB_2O_6 from the reaction between U_3O_8 and B_2O_3 (see reaction 3).

The fact that U_3O_8 and UO_2 diffraction peaks could be observed at the same temperature indicates that the oxidation of UB_2 (reaction 1) and the oxidation of UO_2 (reaction 2) happen simultaneously. UB_2O_6 diffraction peaks were not observed until all UO_2 peaks disappeared, following oxidation at high temperatures. Therefore, the two DSC signals observed during the oxidation of UB_2 may be attributed to the parallel oxidation of UB_2O_6 (higher temperatures). However, the heat release associated with higher temperature DSC peaks is much greater than those which would indicate the formation of UB_2O_6 , which may indicate that the second DSC peak is associated with the oxidation of UB_2 underneath a protective layer of UO_2 and B_2O_3 .

6. Conclusions

Thermogravimetric analysis of the oxidation of UB₂ in air during heating ramps and isothermal testing experiments and by XRD analysis of the oxidation products were performed to investigate the oxidation behaviour of UB₂. The results show that UB₂ has an on-set oxidation temperature of 807 ± 6 K for samples in fragment form and 799 ± 5 K for finely powdered material. UB₂O₆ was observed to form as the terminal oxidation product of UB₂ at 1173 K.

A thermodynamic model for the U-B-O system was developed and found to be in agreement with the available literature data and with the results of the experiments of the present paper. The theoretically calculated heat released by the oxidation of UB₂ was found to be in good agreement with the DSC measurements, with a calculated value of 9.1 J/mg for the heat released by the oxidation of pure UB₂ to UB₂O₆.

Isothermal testing was used to determine the activation energy of the oxidation of UB_2 , which was estimated to be 380 kJ/mol below 873 K and 25 kJ/mol above 873 K.

Data from the isothermal and ramp testing were found to agree with a model for the oxidation of UB_2 in which a passivating layer of uranium and boron oxides is cyclically formed and disrupted,

likely via the disruption of B_2O_3 . The UO_2 formed on the surface of the UB_2 is oxidised to U_3O_8 alongside the UB_2 oxidation reaction. Following the completion of the UB_2 oxidation to UO_2 and B_2O_3 , UB_2O_6 is formed as a final oxidation product.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Q. Mistarihi: Conceptualization, Formal analysis, Investigation, Writing – original draft. **F. Martini:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **J. Buckley:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **S.C. Middleburgh:** Supervision, Funding acquisition. **T.J. Abram:** Supervision, Funding acquisition. **J. Turner:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Data Availability

Data will be made available on request.

Acknowledgements

Dr Mistarihi and Dr Turner's time on this work was funded by the EPSRC (EP/T004983/1) and conducted using equipment purchased using funding from the Department for Business, Energy and Industrial Strategy. Dr Buckley was funded through the Department for Business, Energy and Industrial Strategy's AMR Programme. Prof Middleburgh is supported through the Sêr Cymru II 80761-BU-103 project by Welsh European Funding Office (WEFO) under the European Regional Development Fund (ERDF). Mr Martini is supported via the KESS II programme and Westinghouse Electric Company.

Credit Author

Statement for "The oxidation of uranium diboride in flowing air atmospheres"

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jnucmat.2023.154417.

References

- [1] E. Kardoulaki, J.T. White, D.D. Byler, D.M. Frazer, A.P. Shivprasad, T.A. Saleh, B. Gong, T. Yao, J. Lian, K.J. McClellan, Thermophysical and mechanical property assessment of UB2 and UB4 sintered via spark plasma sintering, J. Alloys Compd. 818 (2020), doi:10.1016/J.JALLCOM.2019.153216.
- [2] H. Muta, K. Kurosaki, A.E. Masayoshi, U. Ae, S. Yamanaka, Thermal and mechanical properties of uranium nitride prepared by SPS technique, J. Mater. Sci. 43 (2008) 6429–6434, doi:10.1007/s10853-008-2731-x.
- [3] J.R. Lamarsh, Introduction to Nuclear Reactor Theory, American Nuclear Society, 2002.
- [4] G.J. Youinou, R.S. Sen, Impact of accident-tolerant fuels and claddings on the overall fuel cycle: a preliminary systems analysis, Nucl. Technol. 188 (2014) 123–138, doi:10.13182/NT14-22.
- [5] N.R. Brown, A. Aronson, M. Todosow, R. Brito, K.J. McClellan, Neutronic performance of uranium nitride composite fuels in a PWR, Nucl. Eng. Des. 275 (2014) 393–407, doi:10.1016/j.nucengdes.2014.04.040.
- [6] J.T. White, Report on the basic chemistry, microstructure and physical properties of high uranium density boride compounds, Los Alamos Report (LA-UR 15-29507) 2015.

- [7] J. Turner, M.J.J. Schmidt, T.J. Abram, The use of carbon to improve the pressureless sintering of uranium diboride, J. Nucl. Mater. 562 (2022) 153581, doi:10.1016/j.jnucmat.2022.153581.
- [8] J. Turner, T. Abram, Steam performance of UB2/U3Si2 composite fuel pellets, compared to U3Si2 reference behaviour, J. Nucl. Mater. 529 (2020) 151919, doi:10.1016/j.jnucmat.2019.151919.
- [9] J. Turner, J. Buckley, R.N. Worth, M. Salata-Barnett, M.J.J. Schmidt, T.J. Abram, UN-UB2 Composite fuel material; improved water tolerance with integral burnable absorber, J. Nucl. Mater. 559 (2022) 153471, doi:10.1016/J.JNUCMAT. 2021.153471.
- [10] J. Turner, F. Martini, J. Buckley, G. Phillips, S.C. Middleburgh, T.J. Abram, Synthesis of candidate advanced technology fuel: uranium diboride (UB2) via carbo/borothermic reduction of UO2, J. Nucl. Mater. 540 (2020) 152388, doi:10. 1016/j.jnucmat.2020.152388.
- [11] M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, JANAF thermochemical tables, 4 (1998).
- [12] P.Y. Chevalier, E. Fischer, Thermodynamic modelling of the C-U and B-U binary systems, J. Nucl. Mater. 288 (2001) 100–129, doi:10.1016/S0022-3115(00) 00713-3.
- [13] J.K. Fink, Thermophysical properties of uranium dioxide, J. Nucl. Mater. 279 (2000) 1–18, doi:10.1016/S0022-3115(99)00273-1.
- [14] A. Navrotsky, T. Shvareva, X. Guo, P.C. Burns, Uranium Thermodynamics of Uranium Minerals and Related Materials, in: Uranium - Cradle to Grave, Winnipeg, Manitoba, 2013.
- [15] I. Hideaki, S. Hisashi, N. Keiji, Lambda-type heat capacity anomalies in U308, J. Nucl. Mater. 64 (1977) 66–70, doi:10.1016/0022-3115(77)90009-5.
- [16] N.G. Chernorukov, N.N. Smirnova, A.V. Knyazev, M.N. Marochkina, A.V. Ershova, The thermodynamic properties of uranyl metaborate, Russ. J. Phys. Chem. 80 (2006) 1915–1919, doi:10.1134/S0036024406120089.
- [17] G. Rousseau, L. Desgranges, F. Charlot, N. Millot, J.C. Nièpce, M. Pijolat, F. Valdivieso, G. Baldinozzi, J.F. Bérar, A detailed study of UO2 to U308 oxidation phases and the associated rate-limiting steps, J. Nucl. Mater. 355 (2006) 10– 20, doi:10.1016/J.JNUCMAT.2006.03.015.

- [18] H. Guo, J. Wang, D. Chen, W. Tian, S. Cao, D. Chen, C. Tan, Q. Deng, Z. Qin, Boro/carbothermal reduction synthesis of uranium tetraboride and its oxidation behavior in dry air, J. Am. Ceram. Soc. 102 (2019) 1049–1056, doi:10.1111/ jace.15987.
- [19] H.R. Hoekstra, Uranyl metaborate and sodium uranyl borate, (1967) 320–330. https://doi.org/10.1021/ba-1967-0071.ch023.
- [20] P.E. Blackburn, Oxygen pressures over fast breeder reactor fuel (I) a model for UO2±x, J. Nucl. Mater. 46 (1973) 244–252, doi:10.1016/0022-3115(73)90038-X.
- [21] E. Kardoulaki, D.M. Frazer, J.T. White, U. Carvajal, A.T. Nelson, D.D. Byler, T.A. Saleh, B. Gong, T. Yao, J. Lian, K.J. McClellan, Fabrication and thermophysical properties of UO2-UB2 and UO2-UB4 composites sintered via spark plasma sintering, J. Nucl. Mater. 544 (2021) 152690, doi:10.1016/j.jnucmat. 2020.152690.
- [22] D.L. Hildenbrand, W.F. Hall, N.D. Potter, Thermodynamics of vaporization of lithium oxide, boric oxide, and lithium metaborate, J. Chem. Phys. 39 (1963) 296, doi:10.1063/1.1734245.
- [23] K.G. Nickel, Corrosion of advanced ceramics: measurement and modelling, 1993.
- [24] E.S. Wood, J. Vandegrift, B. Jaques, Steam oxidation in accident conditions, Compr. Nucl. Mater. Second Ed. (2020) 452–473, doi:10.1016/ B978-0-12-803581-8.11623-6.
- [25] W.G. Fahrenholtz, G.E. Hilmas, Oxidation of ultra-high temperature transition metal diboride ceramics, Int. Mater. Rev. 57 (2012) 61–72, doi:10.1179/ 1743280411Y.0000000012.
- [26] M.L. Whittaker, H.Y. Sohn, R.A. Cutler, Oxidation kinetics of aluminum diboride, J. Solid State Chem. 207 (2013) 163–169, doi:10.1016/j.jssc.2013.09.028.
- [27] Y. Guo, W. Zhang, D. Yang, R.L. Yao, Decomposition and oxidation of magnesium diboride, J. Am. Ceram. Soc. 95 (2012) 754–759, doi:10.1111/j.1551-2916. 2011.04998.x.
- [28] C.E. Holcombe, D.H. Johnson, Characterization of uranium borate (UB2O6) crystals, J. Cryst. Growth. 49 (1980) 207–210, doi:10.1016/0022-0248(80)90085-8.