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Synthesis of Candidate Advanced Technology Fuel: Uranium Diboride (UB₂) via Carbo/Borothermic Reduction of UO₂

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Abstract

The synthesis of uranium diboride (UB₂) from uranium dioxide (UO₂) has been carried out for the first time after a coordinated experimental and theoretical investigation. The reliable conversion of UO₂ to UB₂ is of importance when considering commercially relevant products (e.g. as an advanced technology fuel - ATF), avoiding the use of uranium metal as a reactant. UO₂ was reduced and borated in-situ through careful combination with boron carbide (B₄C) and graphite (carbo/borothermic reduction). The reaction is observed to only be favourable at low partial pressures of CO, here made possible through use of a vacuum furnace at temperatures up to 1800 °C. At higher partial pressures of CO, the product of the reaction is UB₄. For phase pure UB₂, excess B₄C is required due to the formation of volatile boron oxides that are released from the reaction mixture as is observed when synthesising other borides through similar routes.

Keywords: Nuclear, Fuel, Uranium, High Density Fuels

1. Introduction

Uranium diboride (UB₂) is a refractory ceramic with physical properties that make it a promising candidate for the development of high-performance nuclear materials, including fuel. UB₂ has a higher uranium density compared to uranium dioxide (11.68 g cm⁻³ and 9.67 g cm⁻³, respectively [1]), similar to other accident tolerant fuels/advanced technology candidate fuels (ATFs) such as U₃Si₂ (11.31 g cm⁻³ [2]). UB₂ also has a much higher thermal conductivity compared to UO₂ [3, 4], which will result in a lower fuel centre-line temperatures during normal operating conditions and a significantly flatter temperature profile across the pellet. This has a number of beneficial effects: (1) reducing the rate of the temperature-dependent release of fission products, (2) reduction in the pellet strain as a result of thermal expansion (which is similar to that of UO₂), (3) a reduction in the amount of thermal energy stored inside the fuel and importantly (4) a significant increase in the margin to centre-line melting.

At the same time, a higher spatial density of uranium allows more fissile material to be loaded for a given core layout - thereby extending the interval between refuelling outages and improving the fuel-cycle economics. Similarly, UB₂ can be used as a burnable absorber material further improving the fissile content within a core, extending residence times and again improving fuel-cycle economics.

18 Borides have historically not been explored as fuel materials, due to the high neutron absorp-
19 tion cross section of boron-10, which comprises approximately 20 at.% of boron found naturally.
20 The enrichment of boron to increase boron-10 content for use in nuclear control systems is well
21 established, while relatively isotopically pure boron-11 is used in a number of electronic compo-
22 nents that require stability in a radiation environment [5]. There therefore exist industrial-scale
23 methods for isotopic enrichment of elemental boron, albeit potentially not at the scale required
24 for fuel manufacture at present.

25 A key challenge to developing an alternative to UO_2 is that of synthesis and fabrication. UO_2
26 has a number of economical and scalable synthesis routes (including the integrated dry route
27 [6] and wet routes, for example the AUC process [7]) converting uranium hexafluoride (UF_6)
28 to UO_2 . Difficulty identifying a route for conversion either from fluoride or from oxide starting
29 materials (widely available and relatively easy to handle) has dampened the enthusiasm for other
30 ATF candidate fuels, including U_3Si_2 .

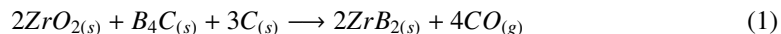
31 Presently, the only reported route for UB_2 preparation is by melting elemental uranium and
32 boron in stoichiometric amounts [3, 8, 9, 10, 32]. This procedure is only suitable for the prepara-
33 tion of small quantities of uranium diboride in a laboratory setting, (uranium powder is py-
34 rophoric and not economical to produce). It must also be noted that the precipitation of uranium
35 diboride from melts of uranium and boron affords products with significant compositional in-
36 homogeneity [3] that would require multiple cycles of solidification, crushing and remelting to
37 achieve a consistent stoichiometry throughout the sample. UB_4 was also produced by fused-salt
38 electrolysis methods, for example in studies by Andrieux [36].

39 The development of an alternative, safer and more reliable route could allow larger amounts
40 of UB_2 to be available for testing and evaluation. In particular, it would be highly desirable
41 to use uranium dioxide as a precursor owing to the wealth of industrial experience and well-
42 established techniques regarding its preparation and handling. Past work has used B_2O_3 or B_4C
43 with an oxide that is then reduced at elevated temperatures forming the desired boride phase
44 [37, 38, 39, 40, 41].

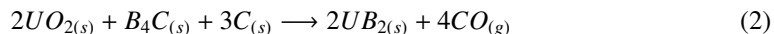
45 The purpose of the present work is therefore to demonstrate that UB_2 may be synthesised
46 through a carbo/borothermic route from a UO_2 precursor, avoiding the need for uranium metal
47 fabrication and/or high temperature melting. It consists of a theoretical thermodynamics study
48 on the required conditions and reactions for UB_2 formation, and experimental demonstration of
49 UB_2 synthesis through the theoretical route.

50 2. Theory

51 The concept of carbo/borothermic reduction has long been applied in the industrial synthesis
52 of diboride ceramics such as zirconium diboride (ZrB_2) [11], which is isostructural with UB_2
53 and has a similar chemistry [12].



54 By analogy, the borocarbothermal route may be extended to the preparation of UB_2 .



55 An excess of boron is typically required in the starting material of this route, due to the
56 presence of relatively volatile boron species in the reaction system [13]. The active removal of
57 carbon monoxide can be used to make reaction 2 more favourable.

58 A thermodynamic evaluation of the reactions was carried out to determine the conditions
 59 under which they may occur. In its most general form, the Gibbs free energy depends on tem-
 60 perature and pressure. In the present case the effect of pressure on the condensed phases was
 61 assumed to be negligible and the pressure sensitivity was wholly ascribed to gaseous CO, allow-
 62 ing us to write:

$$\Delta G_{RXN}(p_{CO}, T) = \Delta H_{RXN}^{\ominus}(T) - T \cdot \Delta S_{RXN}^{\ominus}(T) + C_{CO} \cdot RT \cdot \ln\left(\frac{p_{CO}}{p^{\ominus}}\right) \quad (3)$$

63 Where $\Delta G_{RXN}(p_{CO}, T)$ is the variation in Gibbs free energy at a given temperature T and a
 64 given partial pressure of carbon monoxide in the headspace p_{CO} , $\Delta H_{RXN}^{\ominus}(T)$ and $\Delta S_{RXN}^{\ominus}(T)$ are
 65 respectively the standard variations in enthalpy and entropy at a given temperature, C_{CO} is the
 66 stoichiometric coefficient with which CO is featured in the reaction and p^{\ominus} is the standard state
 67 pressure of 1 bar.

68 3. Thermodynamic Modelling

69 The thermodynamic properties of most of the substances involved in the reaction model
 70 described are widely reported in literature and were immediately available through the NIST
 71 database. Data for UO_2 was taken from [35] and [23] as representative data from the extensive
 72 literature on the material. Conversely, the thermodynamic properties of UB_2 and UB_4 are not
 73 readily available and as such we have used quantum mechanical calculations based on density
 74 functional theory to complement the available data for those compounds, providing a robust set
 75 of predictions relevant to the synthesis of UB_2 . Table 1 summarises the available literature data
 76 on the compounds of interest.

Table 1: Available literature data on compounds of interest. Data for diboron trioxide are referred to its liquid state, since the synthesis takes place above its melting point of 723 K [20].

Substance	$\Delta_f H^{\ominus}$ at 298 K (kJ/mol)	S^{\ominus} at 298 K (J/mol·K)	Other data
$B_2O_3(l)$	-1253.36 [20]	78.45 [20]	$C_p(T)$ function [20]
$B_4C(s)$	-62.68 [20]	26.77 [20]	$C_p(T)$ function [20]
$C(s)$	0.00	5.74 [35]	$C_p(T)$ function [21]
$CO(g)$	-110.53 [20]	197.66 [20]	$C_p(T)$ function [20]
$UB_2(s)$	-164.85 [10]	55.1 [10]	$C_p(T)$ function [30]
$UB_4(s)$	-234.18 [30], -245.60 [22]	68.41 [30] 71.13, [22]	$C_p(T)$ function [30]
$UO_2(s)$	-1085.0 [35]	77.03 [35]	$C_p(T)$ function [23]

77 The enthalpy and the entropy of formation of UB_2 and UB_4 as functions of temperature were
 78 estimated via density functional theory (DFT) calculations, performed with the Vienna ab-initio
 79 simulation package (VASP) [14, 15, 16] and Phonopy [17].

80 For the VASP calculations, the projector augmented wave (PAW) potentials [18] were used in
 81 conjunction with the generalised gradient approximation (GGA) exchange correlation functional
 82 described by Perdew, Burke and Ernzerhof [19].

83 VASP was used to calculate the total energy per formula unit of crystalline structures of α -U
 84 [29], B [28], UB_2 [8] and UB_4 [8] under constant pressure, allowing cell size, shape and volume
 85 to change. Subsequently, Phonopy was used to determine the heat capacity at constant pressure
 86 per formula unit for the substances of interest.

87 In all calculations a convergence threshold of 10^{-8} eV was set for electronic minimisation,
 88 and a threshold of 10^{-7} eV/Å was set for geometric optimisation. The cut-off energy was set to
 89 550 eV for all calculations with a Gaussian smearing of 0.08 eV. A Γ -centred k -point mesh was
 90 automatically generated with a constant k -point density of approximately 0.03 Å³ for each cell.
 91 Convergence tests were carried out with respect to the cut-off energy and the k -point density until
 92 subsequent increases resulted in changes that were smaller than 1 meV/atom. A convergence test
 93 of the smearing parameter σ was carried out by increasing its value and stopping at the maximum
 94 value which resulted in a difference between the total electronic energy and the electronic free
 95 energy smaller than 1 meV/atom.

96 No Hubbard correction was applied to account for electron localisation in U, UB₂ and UB₄,
 97 since elemental uranium is metallic and experimental and computational data show UB₂ [24, 25]
 98 and UB₄ [25] to have no gap between the valence and the conduction band. This is consistent
 99 with the investigations of Burr et al. [1].

100 The static (0 K) formation enthalpy ($\Delta_f H_{i,DFT}$) is simply predicted using DFT. To calculate
 101 the enthalpy of formation at a given temperature T ($\Delta_f H_i(T)$) it is possible to use equation 4:

$$\Delta_f H_i(T) = \Delta_f H_{i,DFT} - q_r(T) + q_p(T) \quad (4)$$

102 Where $q_R(T)$ and $q_P(T)$ represent the heat exchanged respectively by the reactants and the prod-
 103 ucts between 0 K and the temperature T , which can be calculated by integrating their heat capac-
 104 ities over the same range.

105 The literature value for the integral of the heat capacity of UB₂ in the 0-298 K range is
 106 reported by Flotow to be 8.880 ± 0.017 kJ/mol [10], while the value calculated via DFT is 8.557
 107 kJ/mol.

108 The values for the molar entropies $S_i(T)$ of UB₂ and UB₄ were calculated by exploiting the
 109 integral definition of entropy (5), with their entropy at 0 K assumed to be nil according to the
 110 Third Law of thermodynamics:

$$S_i(T) = S_i(0K) + \int_{0K}^{298K} \frac{C_{p,i}(T')}{T'} \cdot dT \quad (5)$$

111 The calculations yield results that are very consistent with the values obtained by experiment
 112 for UB₂ and UB₄ as shown in Table 2:

Table 2: Comparison between the values of enthalpy ($\Delta_f H$) and entropy (S) for UB₂ and UB₄ calculated in this work and those reported in the literature. Values for UB₄ reported in [30] and [22] were close but different (no uncertainties of the measurement were provided) and as such they were averaged and the uncertainty was estimated as the standard deviation between the reported measurements in this study.

Compound	$\Delta_f H$ (298 K) (kJ/mol)		S (298 K) (J/mol·K)	
	This Work	Literature	This Work	Literature
UB ₂	-169.6	-165 ± 17 [10]	55.8	55.1 ± 0.1 [10]
UB ₄	-245.7	-240±8 [22, 30]	67.8	69.8 ± 1.4 [22, 30]

113 The available data on enthalpies, entropies and heat capacities were combined to predict the
 114 behaviour of the reaction system as a function of temperature and partial pressure of CO. The
 115 molar enthalpy of formation $\Delta_f H_i(T)$ and standard molar entropy $S_i^\ominus(T)$ for a substance i at a
 116 given temperature T were calculated according to equation 6 and 7:

$$\Delta_f H_i(T) = \Delta_f H_i(298K) + \int_{298K}^T C_{p,i}(T') \cdot dT' \quad (6)$$

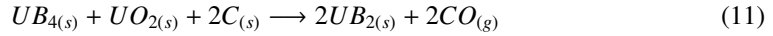
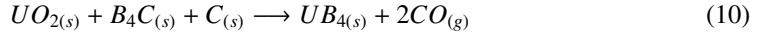
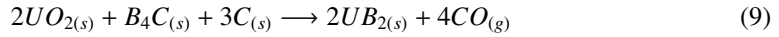
$$S_i^{\ominus}(T) = S_i^{\ominus}(298K) + \int_{298K}^T \frac{C_{p,i}(T')}{T'} \cdot dT' \quad (7)$$

117 Moreover, for CO at a partial pressure p_{CO} a further correction to entropy applies:

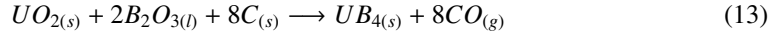
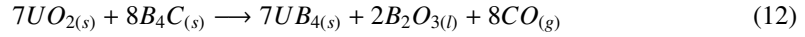
$$S_{CO}(T, p_{CO}) = S_{CO}^{\ominus}(T) - R \cdot \ln \frac{p_{CO}}{p^{\ominus}} \quad (8)$$

118 Where R is the universal gas constant and p^{\ominus} is the standard state pressure expressed in appropriate units (e.g 1 bar).

119 Based on experimental data showing the predominant formation of UB_4 over UB_2 at relatively high partial pressures of CO (see subsequent sections) and on the work of Guo et al. in the preparation of UB_4 [26], calculations were performed for three relevant compositions of the reaction mixture assuming a step-wise behaviour. A mixture prepared according to the stoichiometry dictated by reaction 9 may also host reaction 10, leading to the formation of UB_4 . UB_4 may react further according to reaction 11 to finally afford UB_2 .



128 Reaction 10 may be further split into the two following reactions, which can be favourable in the projected conditions of the synthesis. Reaction 12 indicates a possible pathway for the formation and subsequent loss of volatile $B_2O_{3(l)}$ from the relatively non-volatile B_4C :



131 The calculation of the free energy of formation for the three mixtures reported in Table 3 provides trends such as those reported in Figure 1, here with a p_{CO} of 10^{-4} bar, highlighting the most thermodynamically favourable composition of the mixture as a function of temperature (transitions at 1400 K and 1600 K) - which is the one with the most negative Gibbs free energy (ΔG). Data from these plots can be compiled to provide a phase diagram such as Figure 2, which reports the most stable composition of the solid portion of the reaction mixture as a function of temperature and CO pressure. No reaction occurs in Region 1; only reaction 12 is favourable in Region 2, meaning that any B_2O_3 that forms cannot be converted into other compounds; reaction 10 is favourable in Region 3 but reaction 12 is not, meaning that UB_4 may form via pathways that do not involve B_2O_3 ; both reactions 12 and 13 are favourable in Region 4, allowing UB_4 to form with B_2O_3 as an intermediate product; reaction 11 is favourable in Region 5, finally converting UB_4 into UB_2 . Figure 2 clearly predicted that in order to obtain UB_2 from the borocarbothermal reduction of UO_2 , a region in which UB_4 may form must be initially crossed. As such, it is expected that UB_4 may persist in the final product for kinetic reasons (e.g. non-ideal mixing).

145 As shown by Figure 2, operating at low values of p_{CO} gives a twofold advantage, in that it lowers the temperature at which UB_2 may be obtained and reduces the temperature interval in which UB_4 formation is preferred.

Table 3: Molar ratios of the reaction mixture under the assumption that reactions 10 and 11 proceed to completion

	Initial Mixture	Mixture after Reaction 10	Mixture after Reaction 11
UO ₂	2	1	0
B ₄ C	1	0	0
C	3	2	0
UB ₄	0	1	0
CO	0	2	4
UB ₂	0	0	2

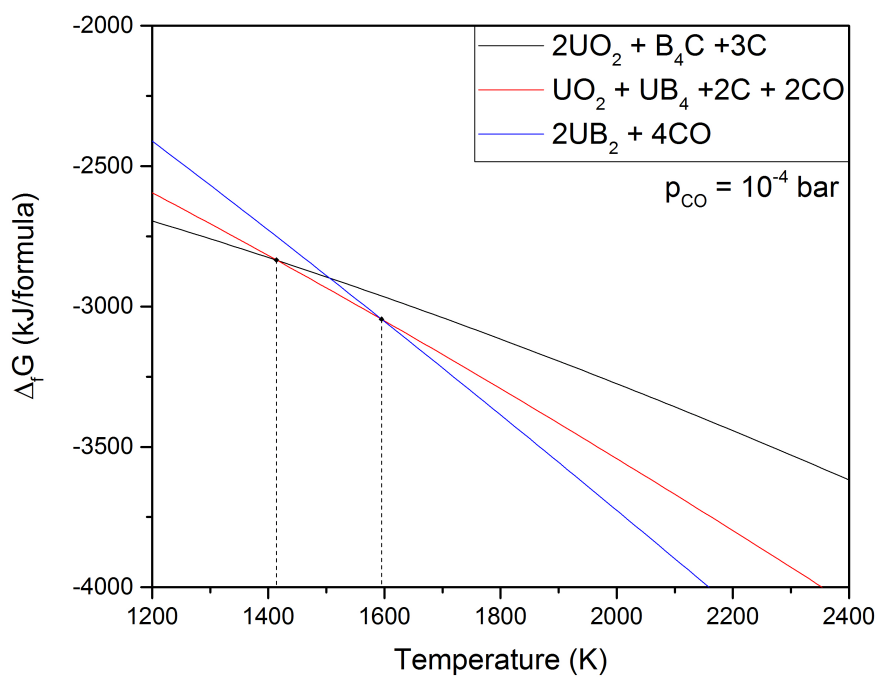


Figure 1: Free energy of formation of the three reactions considered in Table 3, calculated at a CO pressure of 10^{-4} bar

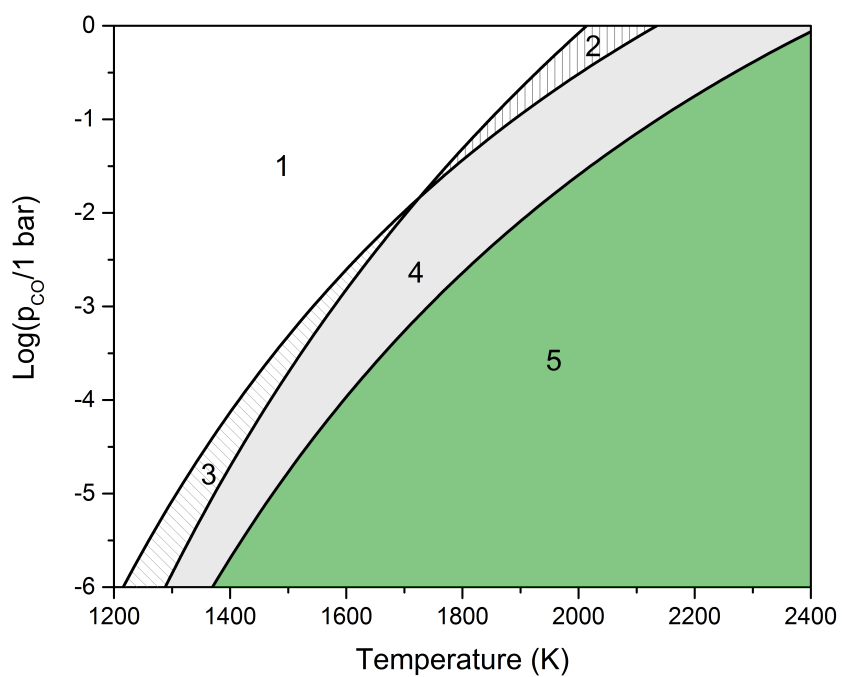


Figure 2: Phase diagram for the condensed phases of the reaction mixture for the borocarbothermal synthesis of UB_2 . Region 1: UO_2 , B_4C and C ; Region 2: UO_2 , UB_4 , B_2O_3 and C ; Region 3: UO_2 , UB_4 and C ; Region 4: UO_2 , UB_4 , C and B_2O_3 may form as an intermediate product; Region 5: UB_2 .

148 4. Experimental Method

149 Synthesis of UB_2 from UO_2 was investigated experimentally by mixing pre-prepared pow-
150 ders according to reaction 2. UO_2 powder was commercially procured from ABSCO ltd (U.K.)
151 and phase purity was confirmed via X-ray diffraction (XRD) prior to mixing, with stoichiome-
152 try measured to be 2.02 ± 0.02 as measured using thermogravimetry. No phases other than UO_2
153 were detected via this method. B_4C was purchased from Sigma Aldrich (99.7% purity), while
154 carbon powder was produced by crushing nuclear graphite (grade NBG-18). Although reaction
155 2 was taken as a reference, exact ratios of carbon and boron carbide were varied in an effort to
156 improve phase purity of the final product, accounting for volatilisation of boron compounds and
157 the production of CO_2 during lower temperature stages of the reaction, as the furnace increased
158 in temperature.

159 Powders were mixed within a planetary ball mill (Retsch PBM 200) using 50 ml tungsten
160 carbide vessels and 10 mm and/or 5 mm media at 350-400 rpm. Milling was carried out for the
161 times listed within Table 4, with reverses of rotation every 10 minutes to ensure a well-mixed
162 powder. Powders were mixed as a blend, carbon or boron carbide added to vary the precursor
163 ratio and then re-milled, and so total milling times are provided within the results presented.
164 XRD performed on blends after milling but before heat treatment did not show the formation
165 of new phases, and it was assumed that there was insufficient energy for mechanically driven
166 conversion.

167 Following milling, powders were pressed at 1 tonne/cm^2 which produced a stable and robust
168 green pellet. Green pellets were heat treated within a graphite crucible on tantalum foil, to
169 prevent additional carbon interaction with the material during synthesis. Initial experiments using
170 alumina crucibles demonstrated that the material reacted with Al_2O_3 to produce a glassy phase
171 (possibly an boro-alumina glass) which physically sealed the crucible lid in one instance.

172 Heat treatment was performed in a Red Devil graphite vacuum furnace (R.D. Webb Red
173 Devil) at 1800°C with a ramp rate of $20^\circ\text{C}/\text{min}$ and a 30 minute dwell time. All runs were
174 started with an initial vacuum (at least 10^{-5} mbar) and operation of the turbo vacuum pump was
175 maintained throughout. As expected, vacuum was seen to vary during operation, likely due to
176 the release of CO during the reaction.

177 Material phase quantification was carried out using XRD (Malvern Panalytical Empyrian).
178 XRD samples of synthesised material were prepared by breaking the pellet within a pestle and
179 mortar, and grinding fragments to a fine powder before sprinkling on a silicon zero background
180 holder. Powder was held in place using Kapton film and petroleum jelly. Phase quantification
181 was carried out using Rietveld analysis, within the Panalytical Highscore programme.

182 5. Experimental Results

183 Initial trials were conducted in flowing Ar at 1475°C with varied compositions and milling
184 parameters. These tests were conducted within an STA, in an effort to observe the onset temper-
185 ature of the reaction, and were not expected to produce phase pure material. However, the only
186 phases produced with these conditions were UB_4 , UC and a UBC phase first reported by Toth et
187 al [27] and are not reported in Table 4.

188 Following heat treatment, mixtures appeared to form semi-sintered pellets which were solid
189 to handle, but could easily be broken if force was applied. The colour of material post-heating
190 varied with the phases present, as confirmed with XRD. UO_2 -rich samples were dark brown or
191 brick red in colour, while UB_2 - and UB_4 -rich material appeared silver or black.

Table 4: Overview of experimental trials. Molar ratio has been normalised to B₄C content. UB₂ content is rounded to $\pm 5\%$ to account for relative inaccuracies within the Reitveld method, as these contents were not corroborated using an alternative method

Reference	Heat Treatment	Milling	UO ₂ Molar Ratio	B ₄ C Molar Ratio	C Molar Ratio	UB ₂ Content	Other Phases
Exp-1	1800C, vacuum	2 hours	2.10	1.00	1.01	30%	UO ₂ , UB ₄
Exp-2	1800C, vacuum	4 hours	2.10	1.00	2.18	70%	UO ₂ , UB ₄
Exp-3	1800C, vacuum	6 hours	2.10	1.00	3.68	85%	UO ₂
Exp-4	1800C, vacuum	30 mins	2.00	1.00	2.50	0%	UB ₄ , C
Exp-5	1800C, vacuum	1 hour	2.00	1.00	3.00	0%	UB ₄ , C
Exp-6	1800C, vacuum	90 mins	2.00	1.00	3.58	90%	UC, UC ₂
Exp-7	1800C, vacuum	4 hours	2.09	1.00	3.04	90%	UO ₂
Exp-8	1800C, vacuum	4 hours	1.86	1.00	2.75	90%	UB ₄ , UO ₂

Table 4 shows the phases synthesised from various heat treatments, milling durations and reactant compositions. XRD spectra of selected products are shown in Figure 3.

Synthesis performed at 1800 °Cs and under vacuum produced UB₂ apart from for Exp. 4 and 5 (although with varied phase purity). Exp. 4 and 5 were milled for comparatively short timescales, 30 and 60 mins, respectively, which may have resulted in poor mixing and therefore a lack of the desired reaction. This is supported by the presence of carbide phases within Exp-6, which do not appear in other experiments. This likely occurs from a localised excess of carbon within the mixture, and a similar mixture milled for much longer (Exp-3) contained residual UO₂, rather than carbides. Residual UO₂ is predicted for well-mixed samples as a result of volatilisation.

The material milled for four hours and containing a relative mixture of approximately 2UO₂:B₄C:3C (Exp. 7) produced 90 % phase pure UB₂ with UO₂ as the only detectable impurity remaining.

The addition of 10 % more carbon and B₄C over that required for reaction 2 (Exp-8) produced the highest purity material, albeit it by a small margin. The UB₂ phase fraction within this material was consistently observed to be between 90 and 92% from repeated XRD analysis, while Exp 7 Experiments typically had 87-89% UB₂ from the same analysis.

6. Summary

The experimental results show that the synthesis of UB₂ from UO₂ is possible with careful consideration of the processing parameters and consideration of intermediate reactions that occur, see reaction 11. The structure of the UB₂ is *P6/mmm* in agreement with previous investigations [3, 32] with a lattice parameter of $\mathbf{a} \equiv \mathbf{b} = 3.133 \text{ \AA}$ and $\mathbf{c} = 3.986 \text{ \AA}$.

Thermodynamic modelling performed in this study suggests that conversion of UO₂ to UB₂ will not occur unless the CO partial pressure is maintained at a sufficiently low value. Experimentally, poor CO removal was observed to result in the production of UB₄ and UBC phases in early trials in flowing argon. Similar behaviour has been reported for ZrB₂ and HfB₂ [33] and more recently for High Entropy Borides (HEBs) [13].

The conversion of the expected initial reaction product, UB₄, to UB₂ appears to be kinetically slow relative to its formation from UO₂. By ensuring the reaction products have a greater degree of intimate contact through thorough milling and mixing, there is a significant reduction in the

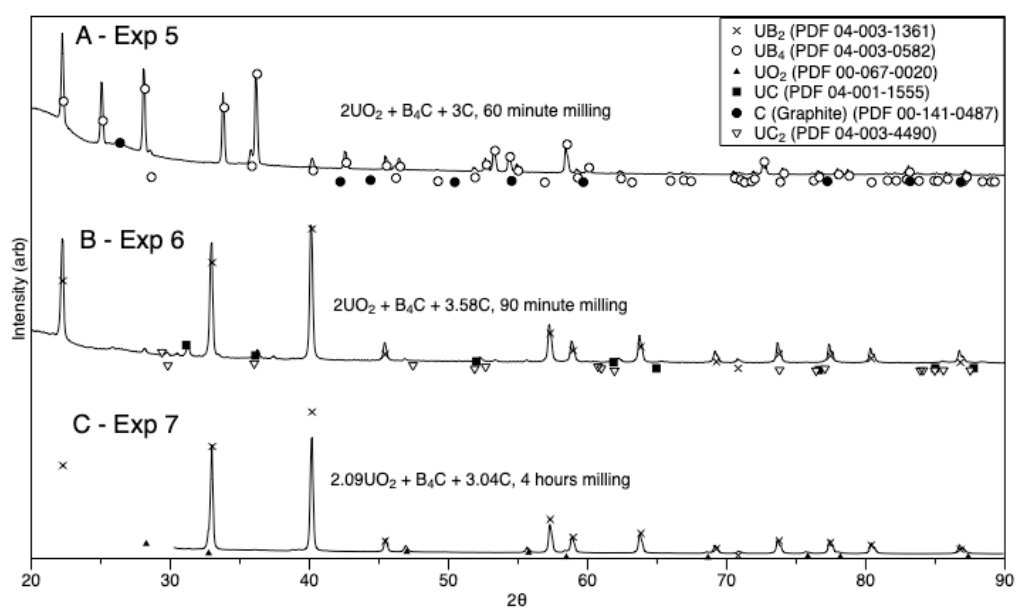


Figure 3: XRD patterns of synthesised material. A: After 60 minutes milling of stoichiometric blend, showing the formation of UB_4 only (Exp-5) B: With additional carbon and 90 minute milling, showing the production of UC alongside UB_2 (Exp-6). C: After four hours milling of stoichiometric blends, showing the synthesis of UB_2 with residual UO_2 (Exp-7). Plotted points correspond to theoretical peak positions and intensities of the reference files listed within the Figure. Data for C was only recorded down to $30^\circ C 2\theta$ due to operator error.

221 impurity phases initially observed (mainly residual UB_4 , carbon and uranium carbide formation).
222 Further work could be considered to improve this mixing further.

223 Finally, the need for additional B_4C within the experiment was anticipated, due to the volatile
224 nature of many boron compounds leading to its loss during fabrication. It is expected that UO_2 or
225 any excess oxygen within the UO_2 will react with B_4C to produce B_2O_3 , a phase that is a liquid
226 above $450^\circ C$ with a very high vapour pressure and therefore volatility [34] (although known to
227 enhance transport phenomena during sintering of compounds such as molybdenum silicide [31]).
228 Any excess oxygen in the UO_2 itself will also need an appropriate amount of either C or B_4C
229 excess to ensure full conversion is possible.

230 7. Data Availability

231 The raw/processed data required to reproduce these findings cannot be shared at this time as
232 the data also forms part of an ongoing study

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