Investigation on boron carbide oxidation for nuclear reactor safety: Experiments in highly oxidising conditions

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Abstract

The oxidation kinetics of boron carbide pellets were investigated in steam/argon mixtures in the temperature range 1200–1800 °C for steam partial pressures between 0.2 and 0.8 bar and total flows (steam + argon) between 2.5 and 10 g/min resulting in gas velocities from 1.01 to 5.34 m/s. A kinetic model for boron carbide pellet oxidation depending on temperature, steam partial pressure and flow velocity is obtained. The activation energy of the oxidation process was determined to be 163 ± 8 kJ/mol. The strong influence of temperature and steam partial pressure on the boron carbide oxidation kinetics is confirmed. The obtained data suggest the coexistence of two kinetic regimes, one at 1200 °C and the other at 1400–1800 °C, with different dependence on steam partial pressure.
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1. Introduction

In French 1300 or 1450 MW pressurised water reactors (PWR), 2/3 of the control rods are made up of boron carbide (B_4C) pellets stacked in a steel tubular cladding, the whole sliding into a Zircaloy (zirconium alloy) guide tube.

The behaviour of this type of rod during the highly improbable event of a core meltdown accident, its influence on how the accident progresses and on the release of radiotoxic products into the atmosphere are still poorly understood, although assumed significant. When the temperature rises in the core during the initial accident phase, the B_4C pellets react with the steel cladding, forming a mix that melts from 1200 °C onwards and which itself reacts with the Zircaloy in the guide tube. This guide tube, which is oxidised by the water vapour at the same time, loses its integrity and leaves the B_4C/steel/Zircaloy mix flowing

down the core. The remaining B_4C pellets, having lost their cladding, and the relocalised mixes will in turn be oxidised by the steam, with two significant and poorly-quantified consequences:

– worsening of material deterioration in the relocalisation zones, caused by the increase in temperature from the heat produced by the oxidation of the mixes and
– production of reaction gases such as hydrogen, carbon dioxide and above all methane which may react with the released iodine to form iodomethane in the cold part of the reactor coolant system. Iodomethane may be a greater contributor than molecular iodine in radioiodine release to the environment because it is difficultly filtered by the sand filters used on the containment venting lines.

The BECARRE program, carried out at the Institut de Radioprotection et de Sûreté Nucléaire (IRSN), is devoted to the study of B_4C rod degradation phenomena in PWR severe accident sequences. The objectives of this programme are improved understanding of the sequence of phenomena in the deterioration of the B_4C control rods

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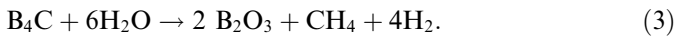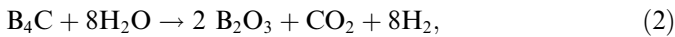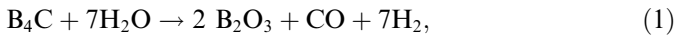*E-mail address:* christina.dominguez@irsn.fr (C. Dominguez).
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and the determination of laws of oxidation of the B_4C pellets and relocalised mixes by steam. These laws will be used to quantify gas production from these reactions to oxidation in order to estimate their potential effect on iodine release into the environment. The results from this programme will serve to improve models implemented in the severe accident codes ASTEC and ICARE/CATHARE developed at IRSN.
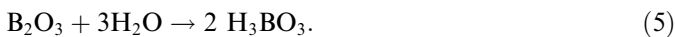
This programme has been initiated in the frame of the COLOSS project [1,2] and will be continued in the frame of the International Source Term programme jointly carried out by IRSN, CEA and EDF. This paper presents and discusses the first series of tests (74) which has been performed with actual B_4C pellets under steam in the VERDI facility. The objective of these tests was to determine a model allowing to simulate the steam oxidation kinetic of B_4C pellets at temperatures typical of a core meltdown accident, that is beyond the cladding rupture temperature (1200 °C). The influence of temperature, gas flow velocity and steam partial pressure in oxidation kinetics was studied. This paper presents the results of these tests. A companion paper [3] presents the modelling that was developed for ASTEC and ICARE/CATHARE codes.

2. Kinetic model of B_4C oxidation under steam in pellet configuration

The oxidation of boron carbide by steam is a complex process that can be determined by the following chemical reactions:

$$B_4C + 7H_2O \rightarrow 2\,B_2O_3 + CO + 7H_2, \tag{1}$$

$$B_4C + 8H_2O \rightarrow 2\,B_2O_3 + CO_2 + 8H_2, \tag{2}$$

$$B_4C + 6H_2O \rightarrow 2\,B_2O_3 + CH_4 + 4H_2. \tag{3}$$

Boron oxide then reacts with steam to form boric acids:

$$B_2O_3 + H_2O \rightarrow 2\,HBO_2, \tag{4}$$

$$B_2O_3 + 3H_2O \rightarrow 2\,H_3BO_3. \tag{5}$$

According to the thermochemical calculation performed by Steinbrück [4], (1) and (4) are the main reactions at temperatures higher than 1200 °C while boron oxide directly evaporates at temperatures above 1500 °C.

The mechanisms that govern the oxidation of B_4C at high temperatures have been largely explained by Steinbrück [4]: the oxidation is controlled by the formation of superficial liquid boron oxide and its loss due to the reaction with surplus steam to volatile boric acids and/or direct evaporation at temperatures above 1500 °C. The formed liquid B_2O_3 covers the pellet surface and acts as a diffusion barrier for the reaction.

The B_4C oxidation rate, defined as the variation of the number of B_4C moles during oxidation, can be expressed as

$$N = -\frac{1}{A} \cdot \frac{dn_{B_4C}}{dt}, \tag{6}$$

where N is the oxidation rate (mol m^{-2} s^{-1}), $\frac{dn_{B_4C}}{dt}$ is the B_4C variation rate (mol s^{-1}) and A is the oxidation surface (m^2).

At temperatures higher than 1100 °C oxidation erodes B_4C pellets, that is, pellet's radius decreases as erosion progresses. If the reduction of section is taken into account to consider the evolution of the surface reaction, N may be expressed, for a B_4C pellet, as

$$N = -\frac{\rho_{B_4C}}{M_{B_4C}} \cdot \frac{dr_{B_4C}}{dt}, \tag{7}$$

where r_{B_4C} is the radius of the remaining B_4C (m), M_{B_4C} the B_4C molar mass (kg/mol) and ρ_{B_4C} the B_4C density (kg/m^3).

The pellet radius evolution during the oxidation process is obtained using Eq. (7):

$$r_{B_4C} = r_{B_4C}^0 - \frac{M_{B_4C}}{\rho_{B_4C}} \cdot N \cdot t, \tag{8}$$

where $r_{B_4C}^0$ is the initial radius of the B_4C pellet and t the oxidation duration (s).

Elrick et al. suggested that the kinetic process responsible for oxidation of B_4C pellets is probably paralinear [5]. The paralinear kinetic model, developed for simultaneous formation and volatilisation of Cr_2O_3 during the oxidation of Cr and Fe–Cr alloys [6], can be expressed by

$$\frac{dy}{dt} = \frac{K_p}{y} + K_1, \tag{9}$$

where dy/dt is the B_4C recession rate (m/s) at time t, $\frac{K_p}{y}$ describes the B_4C parabolic recession due to the formation of a protective B_2O_3 layer and K_1 the B_4C linear recession due to the volatilisation of the B_2O_3 layer. K_p (m^2/s) and K_1 (m/s) are rate constants. As pointed out by Opila [7], K_p varies with partial pressure of the oxidant species and temperature whereas K_1 depends not only on both parameters, but also on gas velocity and total pressure.

In a pellet's geometry, recession can be measured by the radius decrease, so

$$\frac{dy}{dt} = -\frac{dr_{B_4C}}{dt} = \frac{K_p}{r_{B_4C}^0 - r_{B_4C}} + K_1, \tag{10}$$

$$N = \frac{\rho_{B_4C}}{M_{B_4C}} \cdot \left(\frac{K_p}{r_{B_4C}^0 - r_{B_4C}} + K_1 \right). \tag{11}$$

At long times or high volatility rates, a steady state is achieved in which oxide is formed at the same rate it is volatilised. When this steady state is attained, recession rate is linear and directly related to the volatility rate of the oxide [8]. Under conditions at which the volatility rate is much greater than the oxidation rate, nearly linear recession rate is observed, even at short times. Steinbrück [4] observed, at temperatures above 1000 °C, that a constant reaction rate established few minutes after the initiation of the oxidation of boron carbide pellets. Thus the rate of B_4C recession is controlled by the volatility of B_2O_3 rather than by the oxidation rate of B_4C.

Gas transport of volatile boron species is limited by diffusion outwards through a gas boundary layer. Convective mass flux (J in mol m^{-2} s^{-1}) is given by the product of the mass-transfer coefficient (k in m/s) and the density difference of the limiting diffusing species i through the boundary layer:

$$J_i = k \cdot (c_i^s - c_i^b)\rho_i \qquad (12)$$

c_i^b and c_i^s (dimensionless) being the concentrations of species i in the bulk of the fluid and on the surface of the sample and ρ_i (mol/m^3) the density of species i at the considered temperature.

The concentration of the volatile species in the bulk of the fluid is certainly much smaller than that at the surface of the sample and relation (12) may be written

$$J_i = k \cdot c_i^s \cdot \rho_i = k \cdot \frac{P_i}{P} \cdot \rho_i, \qquad (13)$$

where P_i and P are the partial pressure of the volatile species and the total pressure.

Thus, when temperature and total pressure remain constant, the flux of the volatile species linearly depends on the partial pressure of the volatile species:

$$J_i \propto k \cdot P_i. \qquad (14)$$

Sieder and Tate provided the following heat-transfer correlation for a fully developed laminar fluid flow in a pipe, at constant pipe-wall temperature [9]:

$$Nu = 1.86 \, Re^{1/3} Pr^{1/3} \left(\frac{d}{L}\right)^{1/3} \left(\frac{\mu}{\mu_s}\right)^{0.14}, \qquad (15)$$

where Nu, Re and Pr are the Nusselt, Reynolds and Prandtl numbers, d and L are the diameter and length of the pipe and μ and μ_s are the dynamic fluid viscosity at average bulk temperature and at wall temperature. This correlation only applies to short tubes where the entrance effects may be quite significant [9] and is applicable to our situation (cf. Section 3).

The equation of heat-transfer in a pipe (15) can be used to predict mass-transfer coefficients by merely substituting the Nusselt and Prandtl numbers by the Sherwood and Schmidt numbers defined, together with the Reynolds number as follows:

$$Sh = \frac{k \cdot d}{D}, \qquad (16)$$

$$Sc = \frac{\mu}{\rho \cdot D}, \qquad (17)$$

$$Re = \frac{v \cdot \rho \cdot d}{\mu}, \qquad (18)$$

where k is the mass-transfer coefficient, d the hydraulic diameter, D the diffusivity for mass-transfer, μ the dynamic viscosity, ρ the gas density and v the flow velocity. Thus the following mass-transfer correlation is obtained

$$k = 1.86 \left(\frac{D^2 \cdot v}{d \cdot L}\right)^{1/3} \cdot \left(\frac{\mu}{\mu_s}\right)^{0.14}. \qquad (19)$$

The term μ/μ_s is an empirical correction for the distortion of the velocity profile which results from the effect of temperature on viscosity. Because the exponent 0.14 is small, the effect of this term on k is not large and may be disregarded.

Relation (19) clearly shows that the mass-transfer coefficient k in short tubes depends on gas velocity with a 1/3 exponent power law. Consequently relation (14) can be written as

$$J_i \propto v^{1/3} \cdot P_i. \qquad (20)$$

If mass flux is thermally activated following an Arrhenius law:

$$J_i \propto v^{1/3} \cdot P_i \cdot e^{-E_a/R \cdot T}, \qquad (21)$$

where T is the pellet's temperature (K), E_a is the activation energy for gas transport of the limiting diffusing species i through the boundary layer (J/mol), and R is the ideal gas constant.

The partial pressures of the volatile species can be written in terms of the combustion gas phase constituents. Equilibrium constants can be written for reactions (4), (5). For example, when B_2O_3 is liquid:

$$K_4 = \frac{P_{HBO_2}^2}{P_{H_2O}}, \qquad (22)$$

$$K_5 = \frac{P_{H_3BO_3}^2}{P_{H_2O}^3}. \qquad (23)$$

It can be seen from these expressions, that the partial pressures of the volatile species depends on the steam pressure with an exponent. For each volatile species the velocity exponent, that depends on test geometry, is predicted to be 1/3 in short tubes. However, the steam pressure and temperature dependence of each species will vary. Mass flux relation (21) can then be written as

$$J_i \propto v^{1/3} \cdot P_{H_2O}^\beta \cdot e^{-E_a/R \cdot T}, \qquad (24)$$

β being the chemical reaction order.

If the steady state recession rate is limited by gas transport of volatile boron species, the measured oxidation rate can be expressed by the following relation:

$$N = C \cdot v^\gamma \cdot P_{H_2O}^\beta \cdot e^{-E_a/R \cdot T}, \qquad (25)$$

C being a constant. while γ is 1/3 in short tubes. The influence of the parameters T, P_{steam} and v on the boron carbide oxidation rate is obtained from Eq. (25):

$$\ln(N) = \ln C + \gamma \ln(v) + \beta \ln(P_{steam}) - \frac{E_a}{RT}. \qquad (26)$$

That means that plotting $\ln(N)$ as a function of $\ln(v)$, $\ln(P_{steam})$ or $1/RT$ for given values of the other two parameters, allows the determination of the activation energy E_a or coefficients β or γ from the slopes of the curves. For example, E_a can be deduced from the slope of the curve $\ln(N) = \frac{-E_a}{RT} + C'$ when P_{steam} and v are constant.
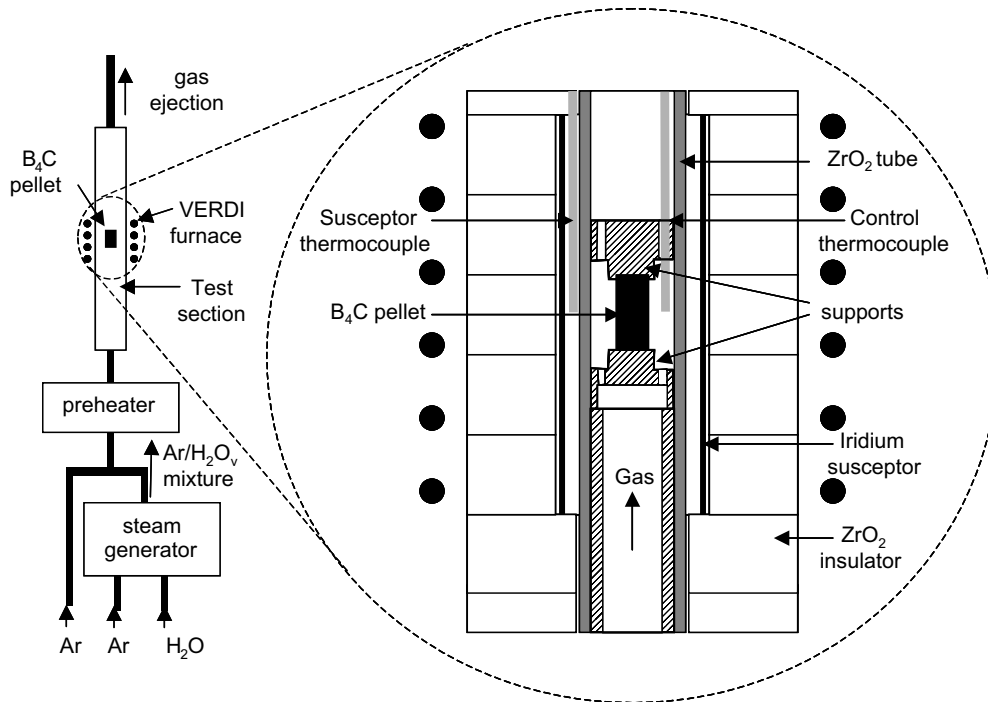
Fig. 1. VERDI test device.

Available data on steam oxidation of boron carbide are highly dependent on samples shape and tests conditions [4,5,10–15]. Up to now, only Steinbrück [4,14] studied French PWR boron carbide pellets. This study was performed mainly at temperatures below 1400 °C and a steam partial pressure of 0.43 bar. Several additional tests were carried out at 1200 °C to study the effect of steam and argon flows (5–70 g/h and 10–90 l/min, respectively) and steam partial pressure (0.11–0.79 bar) on the oxidation kinetics. Total flows were comprised between 0.8 and 3 g/min resulting in gas velocities from 0.09 to 0.26 m/s. Nevertheless, no data exist on the oxidation kinetics of boron carbide at temperatures higher than 1400 °C.

Veshchunov et al. [16] developed the following model for boron carbide oxidation based on Steinbrück tests:

$$N = \left(2.5 \cdot 10^{-7} \cdot e^{\frac{-21600}{RT}} + 6.0 \cdot 10^{5} \cdot e^{\frac{-382900}{RT}} \right) \cdot P_{\text{steam}}, \qquad (27)$$

where the first and second terms in bracket correspond to low and high temperature kinetics, respectively, pointing to a change of the rate determining process (from the formation of gaseous boric acids to direct evaporation of B_2O_3) at temperatures between 1100 and 1200 °C.

Steiner [17], based also on Steinbrück tests, suggested that hydrogen production rate, and consequently boron carbide oxidation rate, should have the following dependence on steam partial pressure and gas velocity:

$$N \propto P_{\text{steam}} \cdot v^{1/2}. \qquad (28)$$

The present study was launched to determine unambiguously the effect of the three parameters (temperature, steam partial pressure and gas velocity) on boron carbide steam oxidation rate and to provide kinetic data on temperatures higher than 1400 °C.

3. Experimental device and procedure

Tests were performed in the VERDI facility. It includes (see Fig. 1):

(1) a gas supply system able to provide pure argon or homogeneous Ar/steam mixtures. To generate Ar/ steam mixtures, two evaporators mixing devices were used:
 – A Serv'instrumentation™ evaporator with maximum steam and argon flows of 16 g/min and 100 l/min (SATP[2]), respectively (equivalent to $Q_{\text{steam}}/(Q_{\text{steam}} + Q_{\text{Ar}})$ rates ranking from 0 to 1). This evaporator must be used with a rotary metering pump. The flow rate accuracies given by the manufacturer are ±0.1 g/min for steam and ±0.3 l/min for argon.
 – an Instrutec™ evaporator with a steam flow between 0.30 and 1.66 g/min and an argon flow between 0.2 and 10 l/min (equivalent to $Q_{\text{steam}}/(Q_{\text{steam}} + Q_{\text{Ar}})$ rates ranking from 0.04 to 0.92). The accuracies given by the manufacturer are ±0.004 g/min and ±0.1 l/ min for steam and argon flow rates, respectively.
(2) A resistive furnace programmed at 800 °C to pre-heat the steam.
(3) An induction furnace to heat the pellet to the desired temperature level.

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[2] Standard Ambient Temperature and Pressure, that is at 25 °C and 1 bar.

(4) a vertical test section (see right part of Fig. 1). The B_4C pellet is located inside a zirconia tube (inner diameter 16 mm, length 300 mm). The assembly design allows direct and homogeneous gas flows at the pellet lateral surface, while upper and lower surfaces of the pellet are protected by zirconia pieces. A thermocouple placed close to the pellet's surface allows to measure fluid temperature. This thermocouple was used to control the test temperature. The distance between the thermocouple and the pellet surface area was less than 1 mm at the beginning of the tests. The test section was thermally insulated over almost its entire length with sections of porous zirconia. The maximum relative uncertainty on temperature measurements is estimated at 1.3% and is linked to potential error on thermocouple positioning during the test. A more detailed description of this experimental test device can be found in an EU report of the COLOSS project [18].

B_4C specimens are standard pellets used in French PWR-1300 (Framatome design). Table 1 summarises pellet's main properties.

The test protocol involves a heat-up phase (20 °C/min) under argon flow, a temperature plateau under a mixture of steam and argon and a final cool-down phase (20 °C/min) under argon flow. As an example, Fig. 2 shows a typical test conduct.

As gas velocity is a parameter that is difficult to control, total mass flow (Q_T in g/min) was used as a test parameter.

Table 1
Sample characteristics

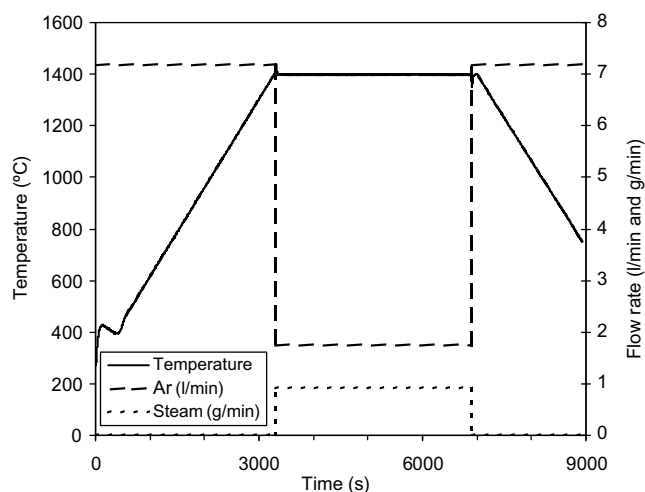| Length	13.9 mm ± 0.2
Diameter	7.47 mm ± 0.05
Density	71% ± 3
	ρ_{th} (B_4C) = 2.52 g/cm^3
B/C atomic ratio	4.0 ± 0.3

Fig. 2. Typical test conduct; here at T 1400 °C, P_{steam} = 0.4 bar, Q_T = 3.97 g/min during 60 min.

Gas velocity depends not only on total mass flow but also on steam partial pressure, temperature and flow section. Flow section (1.57×10^{-4} m^2 at the beginning of oxidation) will increase as oxidation progress due to the consumption of the B_4C pellet. The maximum value of flow section was 2.00×10^{-4} m^2 at the end of the test for the most corroded sample (final sample diameter of 1.3 mm). However, to simplify gas velocity calculation, flow section was considered constant all over the test and equal to 1.57×10^{-4} m^2.

Tests have been performed under the following conditions:

– oxidation temperature between 1200 and 1800 °C,
– oxidation time between 2.5 and 180 min,
– steam partial pressure, P_{steam}, between 0.2 and 0.8 bar and
– total flow (Ar + steam), Q_T, between 2.5 and 10 g/min.

Calculations of the Reynolds number for the experimental configuration gives values ranking from 27 to 223, depending on flow rates, temperature and steam partial pressure, clearly indicative of laminar-flow conditions.

Tests at 1800 °C have been carried out only at low steam partial pressure and low total flow because the oxidation rate was too fast at this temperature.

A test was performed under identical conditions than one of Steinbrück experiments (1400 °C, P_{steam} = 0.43 bar, Q_T = 1.98 g/min and t = 30 min) in order to compare results of both studies. B_4C typical pellet's shape after oxidation in the VERDI facility is shown in Fig. 3. We can observe that oxidation is not homogeneous along the pellet's axis. Upper and lower parts of the pellet are less eroded because these zones are close to the pellet's supports and are less accessible to steam. Thus after the tests, the diameter is constant and minimum only at the pellet's centre (except in samples oxidised at 1800 °C due to steam starvation, cf. Section 4). This minimum diameter was measured by stereomicroscopy with an uncertainty of 0.06 mm (for an initial diameter of 7.47 mm and a minimum one of 1.30 mm).

Due to non-uniform oxidation of pellets, only diameter measurement in the thinner part of the pellet is used to calculate oxidation rate. Pellet mass measurement will lead to underestimate N values.

Initially, it was planned to perform, for each set of values T, P_{steam} and Q_T, three tests with different oxidation times. Nevertheless, in some cases:

– additional tests were performed when obtained experimental results were too largely scattered and
– since the oxidation rate dependency on total flow is low, a single test was carried out in experiments intended to measure the influence of the total flow in oxidation rate.

Tests conduct and results were checked in order to eliminate those that showed experimental problems and those

Fig. 3. Characteristic pellet's shape after oxidation: upper – moderately oxidised pellet at 1200 °C, centre – strongly oxidised pellet at 1400 °C, showing the formation of vitreous drops at pellet's surface and lower – pellet oxidised at 1800 °C.

Fig. 4. Examples of curves showing the evolution of $r(t)$ for given values of T, P_{steam} and Q_T.

4. Experimental results and determination of kinetic constants

Vitreous drops were occasionally observed at the pellet surface after tests at 1200 and 1400 °C (see Fig. 3 central picture). This product is B_2O_3, the liquid formed from the B_4C-steam reaction according to reaction (1) and observed by other authors [4,5,10,11,13,14]. During the tests, a significant release of vapour was noted. A fraction of this product was deposited on the outlet cold walls in the form of a white powder. A XRD analysis revealed that the deposited product is exclusively H_3BO_3 (no HBO_2 was observed).

Two methods were used to determine oxidation rates from pellet's radius measurement:
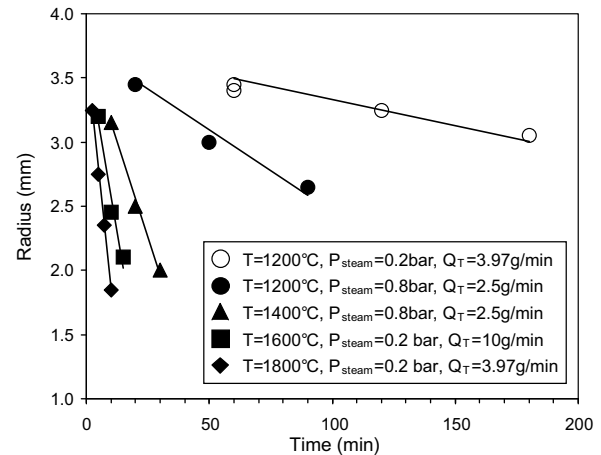
– plotting experimental r_{B_4C} as a function of oxidation time t and applying the least-squares method to calculate N using Eq. (8) (see some examples in Fig. 4). This approach was used when tests with different oxidation times were available for given values of T, P_{steam} and Q_T. This method permits to check the linearity of the r versus t relationship and

– calculating N directly with Eq. (8) when only one test was available.

The γ coefficient in Eq. (25) can be estimated plotting $\ln(N)$ as a function of $\ln(v)$ when T and P_{steam} are constant. The average of the four values plotted in Fig. 5 is $\gamma = 0.29 \pm 0.07$, very close to 1/3, the coefficient predicted for mass-transfer in short tubes (cf. Section 2).

As total flow was used as test parameter instead of gas velocity, the measured N values were corrected to equivalent rates at $v = 1$ m/s using the obtained power law, in order to isolate the effect of temperature or steam partial pressure on the oxidation rate.

The activation energy E_a can be estimated plotting $\ln(N)$ as a function of $1/RT$, when P_{steam} and v are constant (see Fig. 6). The average of the three calculated values is $E_a = 1.63 \pm 0.08 \times 10^5$ J/mol.

Plotting $\ln(N)$ as a function of $\ln(P_{steam})$ when T and v are constant allows to calculate the β coefficient. It can be observed in Fig. 7 that the coefficients deduced at 1400 and 1600 °C (0.39 and 0.42, respectively) are half the one measured at 1200 °C (0.82), suggesting that P_{steam} exponent can be different at low and high temperatures.

That is, two different kinetics laws can be proposed depending on temperature range:

$$k = C_1 \cdot P_{steam}^{0.82} \cdot Q_T^{0.29} \cdot e^{\frac{-163000}{RT}} \quad \text{at 1200 °C,} \tag{29}$$

$$k = C_2 \cdot P_{steam}^{0.41} \cdot Q_T^{0.29} \cdot e^{\frac{-163000}{RT}} \quad \text{between 1400 and 1800 °C.} \tag{30}$$
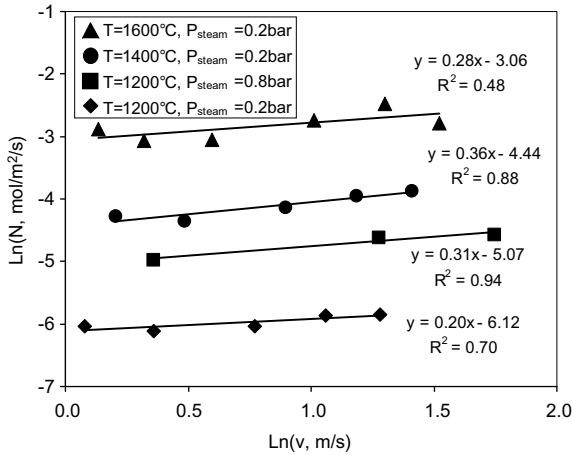
Fig. 5. Kinetic law calculations: $\ln(N)$ as a function of $\ln(v)$ for a selection of tests.
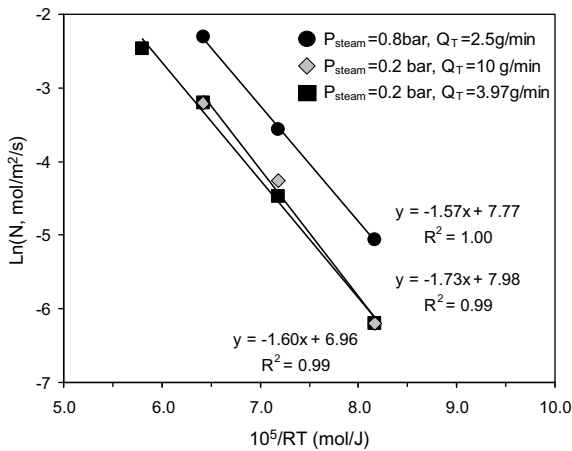

Fig. 6. Kinetic law calculations: $\ln(N)$ as a function of $1/RT$ for a selection of tests. N values corrected to $v = 1$ m/s.
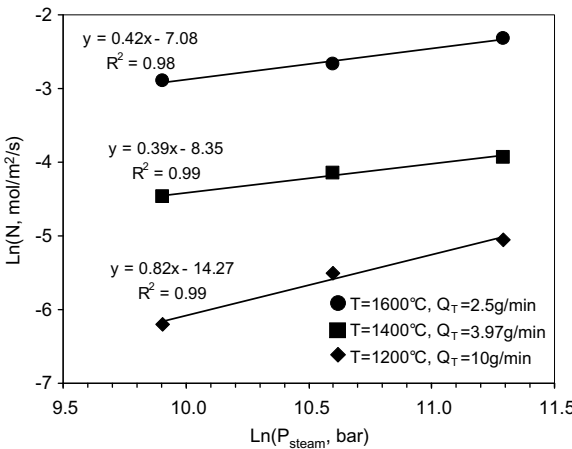

Fig. 7. Kinetic law calculations: $\ln(N)$ as a function of $\ln(P_{steam})$ for a selection of tests. N values corrected to $v = 1$ m/s.

Constants C_1 and C_2 can be, respectively, obtained applying Eq. (29) to oxidation rates measured at 1200 °C and Eq. (30) to oxidation rates measured in the temperature

range 1400–1800 °C. That is, plotting experimental N as a function of $\frac{N_{modelled}}{C} = P_{steam}^{\beta} v^{\gamma} e^{\frac{-E_a}{RT}}$ obtained from estimated values of E_a, β, and γ, and applying the least-squares method to each temperature range to calculate constants C (see Fig. 8).

We obtain $C_1 = 5080$ with a coefficient of determination of 0.96 and $C_2 = 3410$ with a coefficient of determination of 0.94. There is some scatter in the data points but the linear dependence of the data is rather well respected.

Tests at 1800 °C have been carried out only at $P_{steam} = 0.2$ bar and $Q_T = 3.97$ g/min, consequently only one oxidation rate has been measured at this temperature and correspond to the data point of higher $N_{modeled}/C$ value in Fig. 8. It can be observed that the oxidation rate measured at 1800 °C is the one that presents the lower value compared with the modelled value represented by the curve in Fig. 8. The shape of the pellet's oxidised at 1800 °C is irregular (see Fig. 3) with the lower pellet's diameter located close to the gas inlet. This shape can be explained by high steam consumption at the gas inlet due to the fast oxidation rate at this temperature, leading to steam-poor atmospheres downstream. Therefore, steam starvation is responsible of the low oxidation rate measured at 1800 °C. For this reason, the value at 1800 °C has been omitted in the calculation of constant C_2 in Fig. 8.

To estimate the overall fitting of the experimental data by the proposed model, we calculated the discrepancies between N values measured and N values calculated with formulae (29) and (30), that is, the y-coordinate differences between experimental points and regression lines in Fig. 8. The comparison leads to an overall value of relative discrepancy of 26% on the oxidation rate, with a scattering: $\sigma = 18$.

As the measured oxidation is strongly influenced by the thermohydraulic boundary conditions, the obtained laws can only be applied to the studied test conditions, geometry and flow orientation. Nevertheless, excluding the effect of flow velocity that is directly dependent on geometry, the
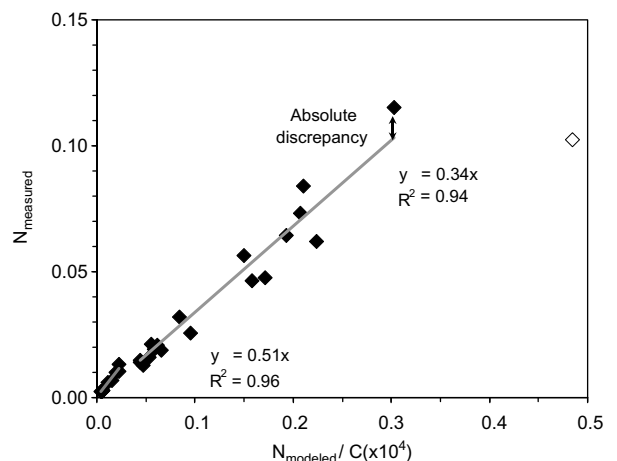

Fig. 8. Calculation of C_1 at 1200 °C and C_2 in the 1400–1600 °C temperature range.

obtained steam pressure exponents and activation energy could be applicable to other tests geometries in the temperature and flow velocity ranges considered by the present study.

5. Discussion

The formation of vitreous B_2O_3 on the pellet's surface and of boric acid in the gas exhaust confirm the oxidation mechanism suggested by different authors [4,5,10], that is B_4C oxidation is controlled by the formation of superficial liquid boron oxide and its loss due to reaction with surplus steam to form volatile boric acids and/or direct evaporation.

The observed H_3BO_3 in the outlet cold walls is not in contradiction with the thermochemical calculation performed by Steinbrück according to which HBO_2 is produced [4]. H_3BO_3 can be formed from the reaction between HBO_2 and steam during transport from the hot reaction zone to the cold outlet.

The results of the comparison test are presented in Table 2 together with FZK results obtained under the same conditions. Pellet's weight loss and oxidation rates determined in the present work are, respectively, 0.25 and two times higher than those obtained by Steinbrück at FZK. Steinbrück measured the hydrogen released in the outlet gases. He observed that oxidation of pellets took place in two steps characterised by a first peak of hydrogen production followed by linear hydrogen production after few minutes [4]. He calculated the oxidation rate in the plateau phase. In the present study, the oxidation rate is estimated by the measurement of the pellet radius after the test. Consequently the present study provides a measurement of the total oxidation, including the initial peak and the constant oxidation phase. From H_2 release measured at 1400 °C in [4], we can estimate that the total oxidation rate, measured in the present study, is 15% higher that the rate of constant oxidation measured by Steinbrück, for a 30 min test. Furthermore, the measurement of the minimum pellet's radius is a local approach that permits to measure the oxidation rate at the pellet's centre, thus avoiding the edge effect. Hydrogen measurement is a more global method that takes into account the oxidation of the entire pellet and should therefore lead to lower rate values. Under highly oxidising conditions, as in the present study, edge effects are significant. Data obtained in the present study avoid bias due to edge effects.

It has been pointed out by Steiner and Veshchunov that the gas flow conditions, mainly the flow velocity field, has a strong influence on the boron carbide oxidation process [16,17]. Test section dimensions where different in both studies leading to different total flow velocities: 0.18 m/s in Steinbrück test compared to 0.95 m/s in the present study. As in the present study oxidation rate depends on flow velocity with an exponent 0.29, an increase in flow velocity from 0.18 to 0.95 m/s will multiply oxidation rate by 1.6. Moreover, the flow velocity field on the specimen surface is additionally modified by the distinct flow-pellet orientation used in both studies. Consequently, even if the distinct measurement methods used can be somewhat responsible, the difference between oxidation rate provided by Steinbrück and the present study can mainly be attributed to the different gas flow velocities.

The activation energy calculated between 1200 °C and 1800 °C is half the one used by Veshchunov at high temperature (from 1200 to 1400 °C) but comparable to values obtained by Sato [12] between 900 and 1300 °C and Liljenzin et al. [15] between 854 and 1055 °C, that are, respectively, 200 and 181 kJ/mol. Due to the few experimental data that Veshchunov had available above 1100 °C, his value at high temperature was evaluated from B_2O_3 evaporation data up to 1000 °C instead of B_4C oxidation data.

The obtained dependence of oxidation rate on thermohydraulic conditions confirms that the transport of gaseous reaction products determines the overall rate in the reaction chain. The coefficients of steam partial pressure and flow velocity obtained in the present study differ from the ones proposed by Steiner and Veshchunov [16,17]. The v coefficient calculated in the present study, 0.29, is very close to 1/3, the coefficient obtained using the heat-transfer correlation provided by Sieder and Tate for laminar fluid flow in short tubes. A coefficient of 0.32 for gas velocity has been obtained in previous tests performed in the same facility with a similar test section [19] confirming that this coefficient depends on test section geometry.

On the other hand, the P_{steam} exponent calculated in the present study at 1200 °C, 0.82, is close to the one proposed by Steiner and Veshchunov for tests performed at this temperature. Nevertheless, the coefficients deduced at 1400 and 1600 °C are half the one measured at 1200 °C, suggesting that P_{steam} exponent can be different at low and high temperatures. A possible explanation of this behaviour can be a change in the species limiting diffusion through the boundary gas layer. A P_{steam} exponent of 0.82 is close to 1, pointing to a reaction mainly limited by the transport of steam inwards through the laminar gaseous boundary layer. A P_{steam} exponent of 0.41 is close to 0.5, consistent with a reaction mainly limited by the transport of formed HBO_2 outwards the gas boundary layer (see reaction (22)).

Furthermore a change in the P_{steam} exponent at a temperature close to 1200 °C agree with the variation in the activation energy observed by Veshchunov between 1100 and 1200 °C. Consequently, there could be a progressive change of the rate determining process at temperatures around 1200 °C. Additional tests would be necessary to

Table 2
Weight loss and oxidation rate measured at IRSN and FZK under the same conditions: French B_4C pellet, $T = 1400$ °C, $P_{steam} = 0.43$ bar, $Q_T = 1.5$ l/min and $t = 30$ min

	Δm (%)	k (mol/m^2 s)
FZK	31	0.0099
IRSN	39	0.021

determine the transition conditions between low and high temperature effects.

6. Conclusions

This series of tests on B_4C pellet oxidation in steam performed in the VERDI facility provides a database that allows the determination of a kinetic model for B_4C pellet oxidation in highly oxidising conditions. Within the tested range of the parameters, temperature between 1200 and 1800 °C, steam partial pressure between 0.2 and 0.8 bar and total flow (Ar + steam) between 2.5 and 10 g/min (corresponding to flow velocities between 1.01 and 5.34 m/s), a model for B_4C oxidation rate is proposed where oxidation is controlled by mass gas-transfer phenomena.

Under the laminar flow conditions and geometry of the tests, the oxidation rate is proportional to the power 1/3 of the fluid velocity. The activation energy of the reaction was determined to be 163 ± 8 kJ/mol. The large influence of temperature and steam partial pressure on the B_4C oxidation kinetics is proven. The obtained results show that the oxidation rate can be estimated by a model where steam partial pressure effect depends on temperature probably due to a change in the species limiting diffusion through the boundary gas layer.

Within the Source Term program, B_4C rod degradation phenomena research will be completed in 2006 and 2007 with the study of the oxidation laws of B_4C/steel mixes and of the degradation of 45 cm-length B_4C control rods contained in their guide tube.

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