

Oxidation of boron carbide at high temperatures

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Abstract

The oxidation kinetics of various types of boron carbides (pellets, powder) were investigated in the temperature range between 1073 and 1873 K. Oxidation rates were measured in transient and isothermal tests by means of mass spectrometric gas analysis. Oxidation of boron carbide 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 1770 K. The overall reaction kinetics is parabolic. Linear oxidation kinetics established soon after the initiation of oxidation under the test conditions described in this report. Oxidation is strongly influenced by the thermohydraulic boundary conditions and in particular by the steam partial pressure and flow rate. On the other hand, the microstructure of the B₄C samples has a limited influence on oxidation. Very low amounts of methane were produced in these tests.

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1. Introduction

Boron carbide is widely used as neutron-absorbing control rod material in boiling water reactors (BWR), Russian RBMKs and VVERs, and in French pressurised water reactors (PWR) where it is applied in hybrid control rods together with a silver–indium–cadmium alloy (SIC). During a hypothetical severe accident, B₄C reacts with the surrounding stainless steel cladding, thus forming eutectic melts at temperatures above 1500 K which are far below the melting temperatures of the single components [1–4]. The remaining uncovered absorber material as well as the B₄C–metal mixtures are exposed to the steam in the reactor core after failure of the control rod.

Oxidation of B₄C by steam is highly exothermic. The amount of hydrogen produced exceeds that generated by the oxidation of the same mass of Zircaloy by a factor of 6–7. Furthermore, gaseous carbon and boron containing species are formed, which may affect the fission product chemistry in the containment. For instance, methane release is of considerable interest because of its potential to produce volatile organic iodine compounds.

The following chemical reactions play a role during oxidation of boron carbide:



Surplus steam then reacts with liquid boron oxide to form volatile boric acids:

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Additionally, boron oxide directly evaporates at high temperatures above 1770 K.

Currently, only a few data sets are available on the oxidation kinetics of boron carbide, most of them have been obtained at temperatures less than 1273 K [5–8]. Only Gogotsi et al. [9] and Sato et al. [10] published results on the oxidation of hot-pressed B_4C pellets up to temperatures of 1473 and 1573 K, respectively. The results of all these tests are mostly based on the evaluation of mass changes. They vary in a wide range and are strongly dependent on the material composition and physical form of the B_4C (pellets or powder) and in particular on the test conditions. No data exist on the oxidation behaviour of sintered B_4C pellets that are typical of PWRs of French design. Therefore, a separate-effects test program on boron carbide oxidation up to 1873 K was launched at Forschungszentrum Karlsruhe (FZK) within the EC COLOSS project under the 5th Framework Programme. It is closely related to the FZK bundle tests QUENCH07 [11] and QUENCH09 [12] with B_4C control rods as well as to the upcoming French Phebus FPT3 test [13]. This paper will describe the results of the extensive experimental work performed with a new experimental set-up. More detailed information can be found in a report published by the Forschungszentrum Karlsruhe [14].

2. Test rig, specimens and experimental procedure

A new test set-up (BOX – Boron carbide OXidation) was constructed and taken into operation at the beginning of the project. The BOX rig (Fig. 1) consists of:

- (1) a gas supply system for Ar, H_2 and steam (0–4 mol/h each) with two gas-flow controllers, one liquid flow controller, and a so-called controlled evaporator mixer unit (CEM), where the liquid water is evaporated and mixed with the non-condensable gas. The whole system was delivered by Bronkhorst High-Tech B.V. (Ruurlo, Netherlands);
- (2) a tube furnace working at maximum temperatures of 2000 K and equipped with an alumina reaction tube (inner diameter: 32 mm, length: 600 mm) and molybdenum heaters, delivered by HTM Reetz GmbH (Berlin, Germany); and
- (3) a quadrupole mass spectrometer (MS) Balzers GAM300 (Balzers, Liechtenstein). All parts of the system are computer-controlled by a LabView program.

The pellet specimens were kept in a specially prepared alumina boat to allow direct and homogeneous access of the steam flow, with an yttria disc as sample support to prevent interactions between pellet and alumina. The powder specimens were kept in a shallow zirconia crucible. The off-gas tube from the furnace to the MS (stainless steel, inner diameter: 6 mm, length:

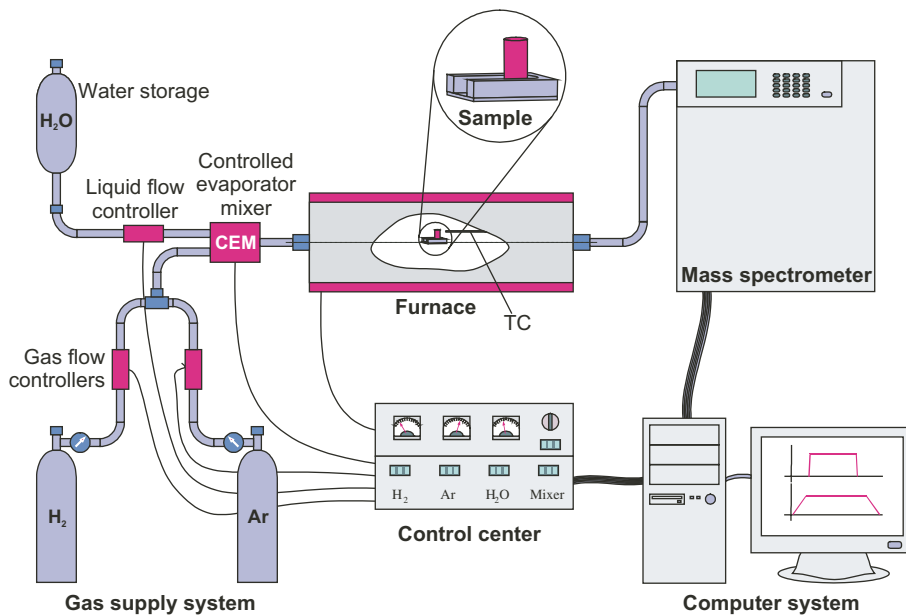


Fig. 1. BOX rig for the investigation of the oxidation kinetics of B_4C .

Table 1
Properties of the B₄C specimens investigated

	Pellet Framatome	Pellet CODEX	Pellet ESK	Powder ESK
Diameter	7.47 mm	7.5 mm	12.25 mm	10.95 mm*
Height	14.0 mm	10.3 mm	9.4 mm	3.0 mm*
Mass	≈1.1 g	≈0.82 g	≈2.6 g	≈0.46 g
Density	1.8 g/cm ³	1.8 g/cm ³	2.34 g/cm ³	1.6 g/cm ³
	71% th.dens.	71% th.dens.	93% th.dens.	63% th.dens.
Open porosity	160 mm ³ /g	110 mm ³ /g	5 mm ³ /g	not measured
	9%	6%	0.3%	
Grain size				14 mesh and finer
Impurities	0.2 wt%	2.3 wt%	0.1 wt%	0.1 wt%

* Inner dimensions of the crucible.

2.7 m) is heated to about 420 K to prevent steam condensation. The mass spectrometer allows for the quantitative analysis of all gaseous reaction products. In particular, the hydrogen release rate was used as a continuous measure of the reaction kinetics in most of the tests.

Four types of B₄C specimens were investigated:

- (1) commercial pellets used in French PWRs (Framatome),
- (2) pellets of Russian origin used in the Hungarian CODEX bundle tests [15] with a boron carbide control rod (CODEX),
- (3) dense absorber pellets without open porosity supplied by Elektroschmelzwerk Kempten, Germany (ESK), and
- (4) B₄C powder (14 mesh and finer) as formerly used in German BWRs and made available by the same company (ESK powder).

The different species were chosen to investigate the influence of the sample state (geometry, density, porosity, surface properties, etc.) on the oxidation behaviour. Table 1 summarises some properties of the different samples. Framatome and CODEX pellets have open porosity, whereas the ESK pellets are dense. The microstructure of the CODEX pellets is much more inhomogeneous than that of the other specimens which is reflected by the high impurity content and a broad pore size distribution.

The specimens were usually heated in an inert atmosphere (50 l/h Ar, NPT) up to the starting temperature desired for transient or isothermal oxidation. Then, steam injection was switched on, usually with a flow rate of 30 g/h. At the end of the oxidation period, steam flow was switched off and argon flow increased to 100 l/h to accelerate gas exchange from oxidising to inert atmosphere, under which the specimens were cooled. As an example, Fig. 2 shows a typical test conduct of isothermal experiments. The steam mass flow rates injected by far exceeded the amount of steam consumed by the oxidation reaction, as can be seen from both steam

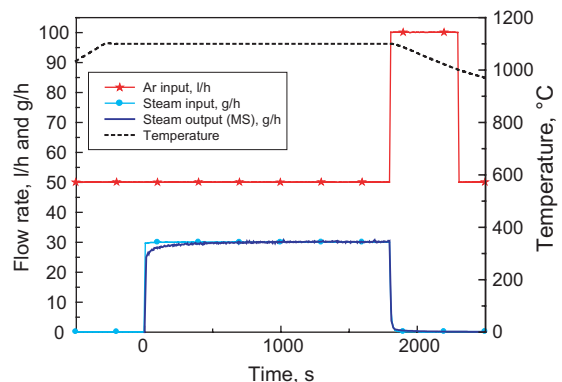


Fig. 2. Typical test conduct of an isothermal test; here: at 1100 °C.

curves (injected, off-gas) in the diagram. Thus, no steam starvation was expected to occur in the tests (including tests at lower steam rates discussed later). The heating rate during heat-up phases and in the transient tests was 20 K/min.

3. Experimental results

3.1. Transient tests

A series of transient tests was performed with Framatome pellets in order to obtain an idea on the reaction behaviour of B₄C in Ar–steam and Ar–steam–H₂ in the temperature range of interest between 1073 and 1773 K. Fig. 3 shows a typical example of gas release during a transient test.

The main gaseous reaction products are hydrogen, carbon dioxide, and carbon monoxide, as it is expected from Eqs. (1) and (2). Only a very small amount of methane was produced in the beginning of the oxidation phase at the lowest temperatures. Taking the hydrogen release rate as a measure of the oxidation rate, Fig. 3 exhibits a strong oxidation peak immediately after steam

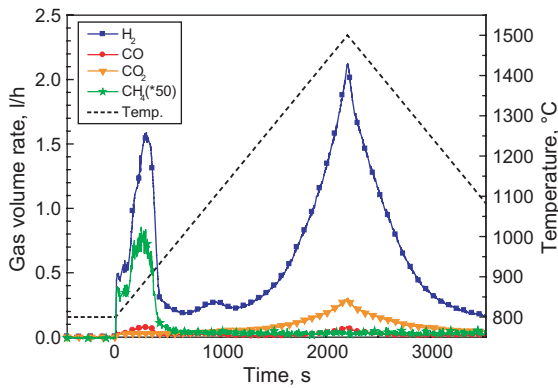


Fig. 3. Gas release during transient oxidation of a B_4C pellet in a flowing argon/steam atmosphere. Measured methane rate is multiplied by a factor of 50.

inlet. Then, the oxidation rate remains roughly constant during heating of the pellet up to temperatures of about 1500 K. With the temperatures further increasing, this rate accelerates again. The first peak will be discussed later in the isothermal section.

Fig. 4 illustrates the dependence of the oxidation rate on temperature in an Arrhenius type diagram. With the initial peak after steam injection and an intermediate peak at about 1370 K, it reveals a complex behaviour that is caused by at least two mechanisms with different dependences on temperature. An exponential Arrhenius type temperature dependence indicating thermal activation of the oxidation reaction is established above approx. 1540 K only.

Two tests were performed in Ar–steam– H_2 mixtures to investigate the influence of the oxygen potential on the composition of the off-gas mixture: one with comparable flow rates of steam and hydrogen and one with a

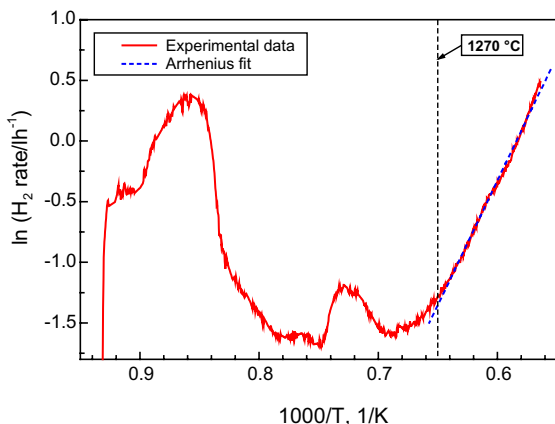


Fig. 4. Dependence of the hydrogen release rate (i.e. B_4C oxidation rate) on temperature.

surplus of hydrogen. Hydrogen injection clearly led to a shift of the CO/CO_2 equilibrium towards CO . The methane release rate was not increased by a reduced oxygen potential. In the test with a surplus of hydrogen, a reduced methane rate was rather caused by a reduced overall oxidation rate due to the lower steam flow (7.5 vs. 25 g/h).

3.2. Isothermal tests

More than 40 isothermal tests were performed with respect to the oxidation of B_4C using different species under various boundary conditions. Most of the tests were performed for 30 min between 1073 and 1673 K under a flowing argon–steam mixture resulting in a steam partial pressure of 0.43 bar (total pressure: 1 bar). An automated procedure allowed for the comparison of various tests.

Most tests were performed with Framatome pellets. These pellets were chosen as reference material, because they are presently used in French nuclear reactors and also employed in separate-effects tests on control rod degradation at FZK [4], out-of-pile QUENCH bundle tests [11,12] as well as in the planned in-pile experiment PHEBUS-FPT3 [13].

Fig. 5(a)–(e) show the results of the mass spectroscopic analysis of the gaseous oxidation products as a function of time and temperature during an isothermal test series. Release of hydrogen, carbon dioxide and carbon monoxide tends to increase with increasing temperature. On the other hand, the highest – but nevertheless low (note the scales!) – methane production was measured at the lowest oxidation temperature. Besides the non-condensable gases, some masses assigned to boric acids (43 and 62 amu) were measured by the mass spectrometer. Boric acids are volatile products of the reaction of B_2O_3 with steam, Eqs. (4) and (5), which is believed to play a significant role in the overall oxidation kinetics. Boric acid production could only be measured qualitatively due to a missing calibration method and partial condensation in the off-gas system. However, Fig. 5(e) indicates that an enhanced production of orthoboric acid H_3BO_3 starts at 1370 K.

Obviously, oxidation of the porous pellets takes place in two steps: a first peak of gas production and, hence, of the oxidation rate is followed by linear oxidation kinetics after a few minutes. Only at 1073 K does the transition from higher to lower oxidation rates take more time.

Comparison of results obtained with the different boron carbide samples at 1473 K provides interesting insights into the oxidation mechanisms. Fig. 6 demonstrates that the initial peak hydrogen production (i.e., oxidation rate) is closely correlated with the porosity of the sample. Strongly increased hydrogen rates after

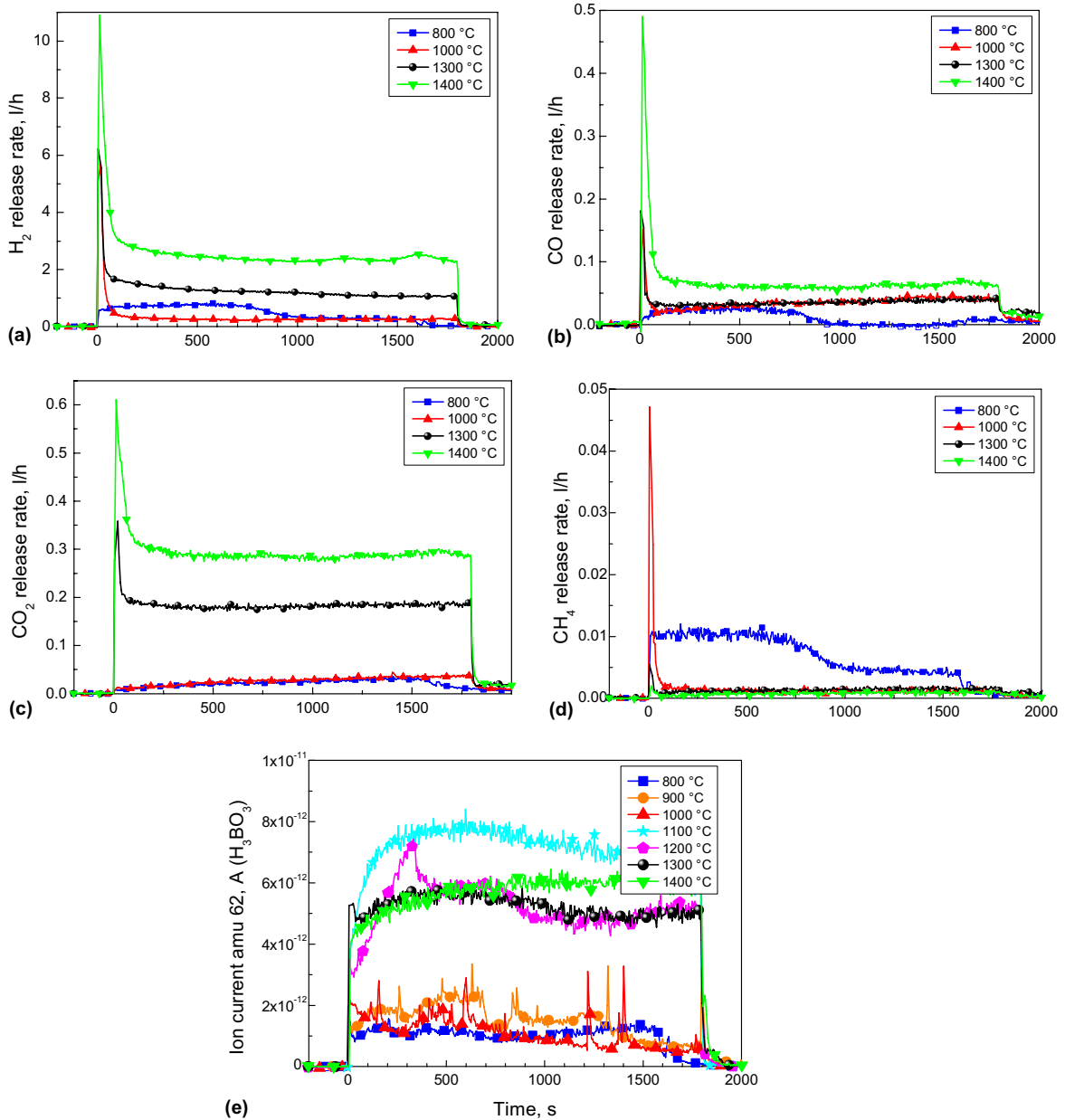


Fig. 5. Gas release during isothermal oxidation of porous boron carbide pellets at selected temperatures.

switching on the steam injection are observed for the porous pellets and the powder (not shown in the diagram) only. A more or less constant oxidation rate is established soon. For the pellets at least, it is only dependent on the steam flow rate or, more generally, on the thermohydraulic boundary conditions. Obviously, the porous specimens initially have a larger active surface area that leads to increased oxidation rates. The liquid boron oxide formed fills or clogs pores. Only the geometric surface area is available for steam access during

the constant phase. In this phase, the oxidation rate is controlled by the transport of boric acids formed by the reaction of B_2O_3 and steam, Eqs. (4) and (5), into the gas phase and at higher temperatures (>1770 K) by direct evaporation of boron oxide.

The somewhat different behaviour of the powder, which gave higher but continuously decreasing specific oxidation rates, can be explained easily by the higher open porosity that yields a larger surface area than the geometric one (to which the data are referred to) and

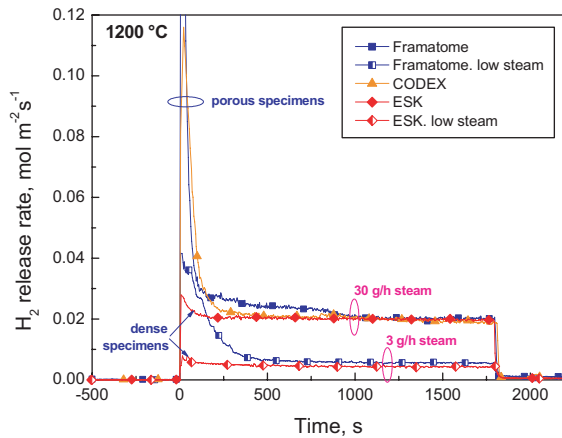


Fig. 6. Specific hydrogen release rates referred to the geometric surface area of the specimen during isothermal oxidation of various B_4C pellets. Influence of porosity and steam flow rate.

which is not completely filled by liquid B_2O_3 during the test.

These ideas are confirmed by the integral mass changes measured for all specimens shown in Fig. 7. At 1073 K, most of the specimens gained mass due to the formation of boron oxide that remained in the pores or on the surface of the sample. At higher temperatures, the boron oxide increasingly reacts with steam and forms volatile boric acids or directly evaporates, as a result of which mass of the specimens is lost. Furthermore, conclusions can be drawn from the comparison of the results obtained for the various species. The ESK pellets without open porosity do not gain mass even at the lower temperatures, and the powder sample with the

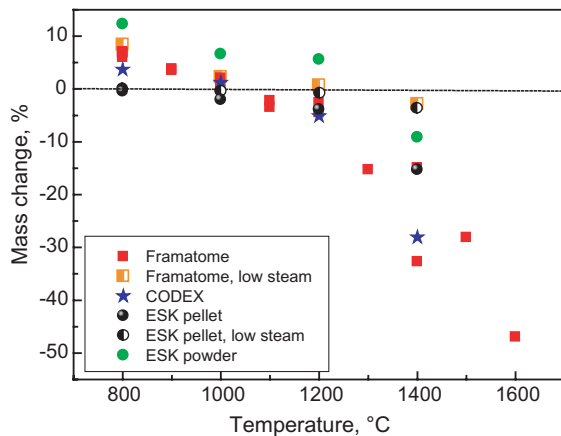


Fig. 7. Integral mass change of B_4C specimens after 30 min oxidation in a flowing steam/argon mixture as a function of temperature. The tests at 800 °C and low steam flow rate took 60 min.

highest porosity experiences the highest increase in mass up to 1473 K. This is associated with a higher capacity of absorbing liquid boron oxide. At 1673 K, the slow oxidation kinetics in the tests at a low steam flow rate caused the lowest mass losses of these specimens.

Post-test X-ray diffraction and scanning electron microscopy revealed superficial boric acid (H_3BO_3) precipitations on porous pellets, especially after the tests at lower temperatures. For dense pellets, even macroscopic superficial boron oxide layers, which were partially relocated to the bottom of the sample, were found after tests at higher temperatures.

3.3. Tests under varying atmospheres

Some tests were performed under varying atmospheres to quantify the effect of gas and steam flow rates on the oxidation kinetics and to investigate its influence on the composition of the gaseous reaction products.

It was of particular interest whether the production of methane could be enforced by atmospheres having a high content of hydrogen and, thus, a low oxygen potential. Two tests were conducted with stepwise changes from a pure steam (incl. argon) to an almost pure hydrogen (incl. argon) atmosphere at 1073 and 1473 K. Reduction of the steam flow rate led to a decrease of the carbon-containing species CO , CO_2 and CH_4 , thus indicating a decrease in the oxidation rate. The change in the oxygen potential did not significantly influence the relative composition of the off-gas. The CO/CO_2 ratio only increased initially with hydrogen injection. As in the transient tests, methane production was not enhanced by the reduced oxygen activity.

Fig. 8(a) and (b) show the results of two tests with a stepwise variation of the steam and argon atmosphere, respectively. The flow rate of the other component was kept constant in each case. The increase in steam flow rate by an order of magnitude (corresponding to an increase in steam partial pressure from 0.11 to 0.64 bar) enhances the oxidation rate (here shown as hydrogen release rate) by a factor of 5. On the other hand, the increase in argon flow rate by an order of magnitude (corresponding to a decrease in steam partial pressure from 0.79 to 0.27 bar) causes a decrease of the oxidation rate by about 30%.

These results reveal that the oxidation rate of boron carbide is strongly influenced by the steam partial pressure and the flow rate of the inlet gas mixture at a given temperature. The two parameters determine the local steam partial pressure on the surface of the specimen and, hence, the oxidation rate. Considering surface reaction kinetics and mass transport in the gas phase, the oxidation rate may be assumed to be proportional to the square root of steam flow rate as well as to the square root of the steam partial pressure at a given temperature [16,17].

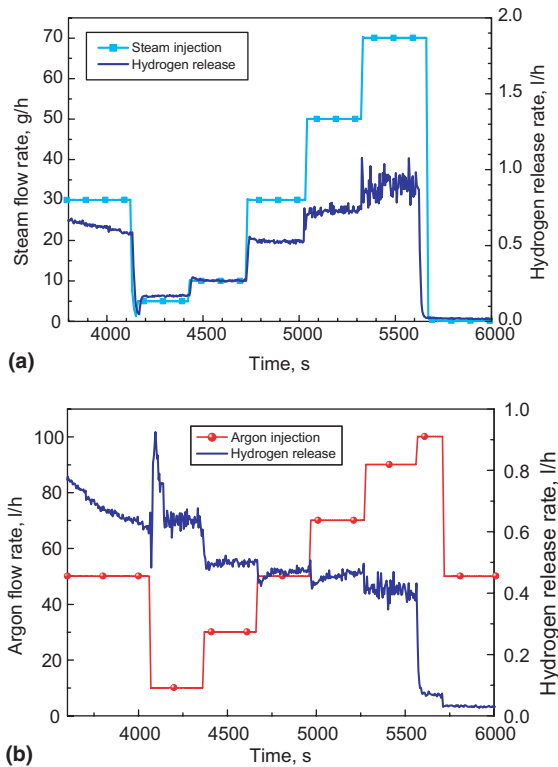


Fig. 8. Boron carbide oxidation rate as a function of the steam flow rate and steam partial pressure at 1200 °C. Argon rate and steam rate, respectively, were kept constant during these tests.

4. Thermochemical calculations

Thermochemical calculations were performed using the equiTherm 5.0 software [18] with the built-in Barin [19] database for pure substances. Oxidation of B_4C in steam-containing environments can be described by the chemical reactions (Eqs. (1)–(5)) given in Section 1.

According to the calculations (Fig. 9), CO production is preferred at higher temperatures. This is in contradiction with the experimental results, according to which CO_2 release, Eq. (2), predominates. Possibly, the CO/CO_2 ratio decreases during transport from the hot reaction zone in the furnace through the 400 K tempered piping to the mass spectrometer. A significant methane production which is of interest due to its potential influence on the iodine fission product chemistry is obtained at low temperatures only (<1000 K). Additional calculations demonstrated that the transition temperature from preferred $CO + CO_2$ production to CH_4 production depends on the oxygen potential in the gas mixture. It is shifted towards higher temperatures with increasing hydrogen content in the off-gas. At temperatures above 1470 K and 1770 K, considerable amounts of gaseous metaboric acid HBO_2 and boric oxide B_2O_3 , respec-

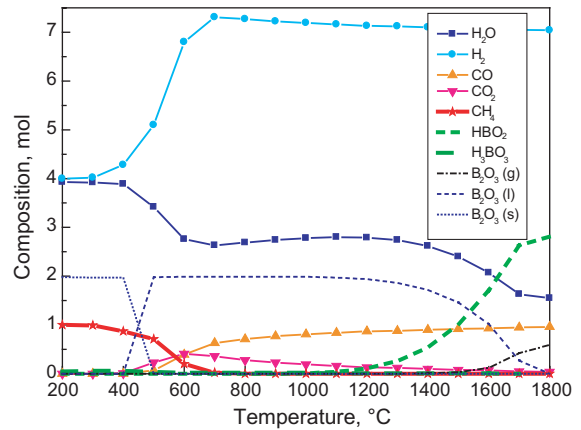


Fig. 9. Thermochemical calculation: equilibrium composition of 1 mole B_4C and 10 moles H_2O as a function of temperature.

tively, are calculated to evaporate. Only a minor influence of system pressure on the composition of the reaction products was found in the calculations.

5. Summary and conclusions

Extensive test series were performed to study the oxidation behaviour of boron carbide at high temperatures. Four types of B_4C specimens with quite different properties were investigated under various atmospheres in the temperature range between 1073 and 1873 K. In contrast to most B_4C oxidation results published in the past, where only the mass change was analysed, the tests described here focused on the release rates of the gaseous reaction products.

The oxidation kinetics of B_4C in steam at the temperatures of interest are supposed to be determined by two processes at least: (1) formation of liquid B_2O_3 which covers the surface and may act as a diffusion barrier for the reaction, and (2) evaporation of B_2O_3 and its reaction products with steam, mainly boric acids. The former process which is only dependent on temperature follows parabolic kinetics, whereas the latter that depends on temperature and thermohydraulic boundary conditions and in particular on the local steam partial pressure at the B_4C /gas interface is of linear kinetics, thus giving a parabolic oxidation kinetics $dx/dt = K_p/x - K_1$ with K_p and K_1 being the parabolic and linear rate constants [20].

Under the conditions chosen in the tests and thought to be existent during severe accidents, a constant reaction rate established soon after the initiation of oxidation. It was mainly dependent on the steam flow conditions. Only during the initial phase was the oxidation kinetics influenced by the microstructure of the specimens, especially by their porosity. It is assumed

that due to different open porosities of the various specimens, the active surface area differs at the beginning of the reaction. Formation of liquid boron oxide soon causes plugging of the pores. Consequently, oxidation may take place at the outer (geometric) surface of the samples only and comparable results are obtained for the various pellet types. Only at low oxidation rates, i.e. at low temperatures and low steam flow rates, does the porosity of the specimens influence the oxidation rate for longer times.

Due to the strong dependence of the oxidation rate on the thermohydraulic boundary conditions, literature data on the oxidation of B_4C scatter considerably and do not allow for any direct comparison. Oxidation rates determined in the present work are compared with literature data in Fig. 10. These values are based on the hydrogen release data during the plateau phase and are related to the geometric surface of the pellets. The FZK data usually were obtained at higher steam partial pressures and rates and, hence, are above the average of the data known from literature. The data obtained at lower steam flow rates are more comparable with Liljenzin's [8] and Sato's [10] results.

A thermally activated temperature dependence following an exponential (Arrhenius type) equation is obtained at temperatures above 1540 K only, as obvious from the transient tests and confirmed by the isothermal experiments. At these temperatures, the oxidation rate seems to be determined by mass transport in the gas phase only. At lower temperatures, the dependence on temperature is much more complex due to the mechanisms described above. For explanation, modelling work is required.

Besides hydrogen, the main gaseous reaction products of the oxidation of B_4C in water vapour-containing atmosphere were carbon dioxide and carbon monoxide.

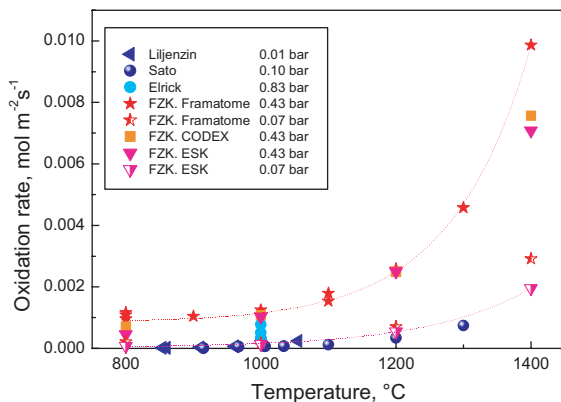


Fig. 10. Oxidation of B_4C at high temperatures: comparison of recent FZK results with literature data obtained under different boundary conditions.

Only very small amounts of methane (CH_4) were released even during the tests at the lowest investigated temperatures of 1073 K. With increasing temperature, the release rates further decreased to almost zero above 1273 K. This is in agreement with the thermochemical calculations which revealed a considerable methane production below 1000 K only.

The experiments gave rise to a number of data which can be used for model development and validation. It was shown that the boundary conditions have a strong influence on the oxidation process and, hence, have to be included in the models. The properties of the specimens themselves hardly affect the oxidation kinetics.

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