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Modeling of boron carbide oxidation in steam

H. Steiner *

Forschungszentrum Karlsruhe, Institut für Materialforschung III, P.O. Box 3640, 76021 Karlsruhe, Germany

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Abstract

A simple parametric model has been developed for the simulation of boron carbide oxidation tests at high temperatures done at Forschungszentrum Karlsruhe. The model predicts that an equilibrium oxide film thickness is reached, whose value is only determined by the two rate parameters of the model. Applying the principles of convective mass transfer in coolant channels, one is able to establish the link from the parametric model to a more generalized consideration, which allows to identify the hydrogen surface concentration as a parameter, which is independent of the flow conditions.

1. Introduction

Boron carbide is used as a neutron absorbing control rod material in Light Water Reactors of various designs. In case of an accident different safety problems arise with these absorber rods. In first instance there occur eutectic reactions between existing materials like stainless steel cladding and B_4C and also stainless steel and Zircaloy above about 950 °C [1,2]. When the steam has free access to the surface of B_4C a distinct exothermic oxidation ensues with formation of highly volatile boric acids.

There have been some experimental investigations on the oxidation of boron carbide done in the past [3–6] at temperatures mostly below 1000 °C. The results of these tests vary in a wide range and are strongly dependent on the material composition and the physical form of the specimens and on the test conditions. The authors in [3–6] recognized the importance of some test parameters like steam partial pressure but ignored the effect of others like flow velocity and system pressure and how the whole test set-up and the flow conditions influence the results.

Different processes take part in the oxidation of boron carbide specimens, namely diffusive processes in the boron carbide itself and in the liquid oxide film, chemical reactions and vaporization processes and last but not least the transport of gaseous reaction products like hydrogen, methane, carbon oxides and boric acids. The rate determining step is most probably after some initial phase, when the equilibrium oxide film thickness has been reached, the transport of these gaseous species, especially boric acid by the fluid, as the slowest mechanism determines the overall rate in a reaction chain. Therefore the flow conditions in the coolant channel, even the whole test set-up are decisive for the oxidation rates.

Recently, a separate-effects test program on boron carbide has been taken up at Forschungszentrum Karlsruhe [7,8] and at Institute de Radioprotection et de Sûreté Nucléaire (IRSN), France. A modeling effort was needed for the support of this test program, as the results on boron carbide oxidation should find

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[*] Tel.: +49 7247 824113; fax: +49 7247 823956.
E-mail address: helmut.steiner@imf.fzk.de

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application in safety codes. In a first step, a parametric model for the BOX tests [7] with single pellets in a cross-flow position of a circular reaction tube in laminar flow and also for the thermo-balance tests [8] will be developed. The importance of the flow conditions is then elucidated with the help of the principles of mass transfer in coolant channels under forced convection flow conditions. This allows us to apply the model also to different flow conditions and under different test environments, for example in the absorber element of an LWR.

Gravity effects are not taken into account. This would complicate the model. Except for low steam partial pressures and low flow velocities the equilibrium oxide film thickness comprises only a few microns (see below). Therefore in most cases one can neglect gravity effects, as for example in the BOX tests [7], whereas in the thermo-balance tests [8] some indications have been found for slumping of the oxide film.

In case of low density material the so-called pore effect is observed. The author assumes that this effect is determined by the steam supply through the pore channels, which occurs by gas diffusion. The pore effect is finished, when the pore channels are closed by oxide film formation.

2. Model development and results

The development of a mechanistic model with all the relevant processes being included seems out of reach as most of the physical parameters, which would be needed for such a model, are unknown. Also, such a model would be rather unwieldy. It is the aim to develop a simple model, which can, in principle, be implemented in safety codes. The basic assumption is that the boron carbide is oxidized under forced convection flow conditions and that pellet specimens and not powder samples are considered.

The oxidation of boron carbide in a steam environment is a complex process. But the experimental data obtained in the BOX tests [7] and also data from QUENCH-07 [9] and QUENCH-09 [10] suggest that CH_4 production is rather unimportant and can be neglected to a first approximation. Therefore, only the main reactions at high temperatures are taken into account:

$$B_4C + (8-x)H_2O \rightarrow 2B_2O_3 + xCO + (1-x)CO_2 + (8-x)H_2 \tag{1}$$

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

For the sake of simplicity in Eq. (1) it is assumed without much loss of generality, that CO and CO_2 are produced at equal parts ($x = 0.5$). Furthermore, it is also assumed that all carbon which is liberated upon boron oxidation is released quantitatively.

2.1. High density material

The author assumes that the evolution of the specific mass of the oxide film m^{ox} can be described by the following balance equation:

$$\frac{dm^{ox}}{dt} = \frac{a^{ox}}{m^{ox}} - b^{ox}, \tag{3}$$

$$m^{ox} = \rho^{ox} \cdot \delta^{ox}, \tag{4}$$

where a^{ox} and b^{ox} are rate parameters, which are to be determined with the help of the experimental data. m^{ox} is the specific mass of the oxide film.

The production rates of boric acid, hydrogen and CO/CO_2 are given as

$$\frac{dm^{b.a.}}{dt} = F^{act} \cdot f_{ox/b.a.} \cdot b^{ox}, \tag{5}$$

$$\frac{dm^{H_2}}{dt} = F^{act} \cdot f_{ox/H_2} \cdot \left(\frac{dm^{ox}}{dt} + b^{ox}\right), \tag{6}$$

$$\frac{dm^{CO/CO_2}}{dt} = F^{act} \cdot f_{ox/CO/CO_2} \cdot \left(\frac{dm^{ox}}{dt} + b^{ox}\right), \tag{7}$$

where ρ^{ox} is the oxide density, δ^{ox} the oxide film thickness, F^{act} the active surface of the specimen, b.a. the boric acid and $f_{ox/b.a./H_2}/CO/CO_2$ are the stoichiometric mass conversion factors.

Eqs. (3) and (5)–(7) are for forced convection flow conditions. Such equations would not apply if tests are done in a closed volume. In this case, according to the mass action law the boric acid partial pressure, for example, would rise with time up to an equilibrium value and then the process would come to a halt. The stoichiometric mass conversion factors in Eqs. (5)–(7) are determined by the reaction scheme given in Eqs. (1) and (2).

The first term on the right-hand side of Eq. (1) describes the oxide formation due to diffusive processes through the oxide film and the second term is a loss rate, which represents either oxide vaporization in dry atmosphere or boric acid formation and transport in wet atmosphere.

It is an experimental fact that the hydrogen flow rates become fairly constant after a certain lapse of time [7]. This is then according to Eq. (6) equivalent to the following equilibrium condition for the oxide film:

$$\frac{dm^{ox}}{dt} = 0. \tag{8}$$

The equilibrium film thickness δ^{ox}_{equ} is then given as

$$\delta^{ox}_{equ} = \frac{a^{ox}}{b^{ox} \cdot \rho^{ox}}. \tag{9}$$

Condition (8) means that the mass increase due to diffusion is just balanced by the loss from the oxide film. In this way, the rate parameter b^{ox} under wet conditions is identified with the oxidation rates measured by different authors [1,3,4].

The rate parameter a^{ox} could be determined with the help of a test done in the thermo-balance in dry atmosphere under a temperature ramp going up to 800 °C [8]. It was found that oxide vaporization was unimportant under these conditions and the measured mass increase was fairly parabolic.

Boric acid is a volatile species and in view of the rather high temperatures, one does not expect that a film of boric acid is deposited on the oxide surface. Therefore, the rate parameter a^{ox} is also valid under wet conditions. But, of course, direct experimental evidence in this respect would be very helpful. The following correlations have been determined from the test data in [7,8]:

$$a^{\mathrm{ox}} = 1.02 \cdot 10^{-4} \cdot \mathrm{e}^{-12\,980/T}, \tag{10}$$

$$T \leqslant 1430\ \mathrm{K} : b^{\mathrm{ox}} = 9.612 \cdot 10^{-4} \cdot \mathrm{e}^{-5190/T},$$

$$T > 1430\ \mathrm{K} : b^{\mathrm{ox}} = 3.62 \cdot \mathrm{e}^{-1.7220/T}. \tag{11}$$

($p_{\mathrm{st}} = 0.43$ bar, $j_{\mathrm{st}} = 30$ g/s, $j_{\mathrm{Ar}} = 50$ L/h).

T in Kelvin, a^{ox} in $\mathrm{g^2/(cm^4\ s)}$, b^{ox} in $\mathrm{g/(cm^2\ s)}$.

The rate parameter b^{ox} describes the loss due to the gaseous reaction products. It depends therefore on the thermohydraulic conditions in the coolant channel and on the atmosphere, especially on the steam partial pressure. This dependence is not yet evident from Eq. (11), as this correlation was obtained for isothermal tests in the BOX Rig [7] with fixed values of the steam and Ar flow rates and therefore fixed values of the steam partial pressure ($p_{\mathrm{st}} = 0.43$ bar) and of the total flow rate. In order to determine how the rate parameter b^{ox} depends on the flow conditions one must make use of the principles of convective mass transfer. This is done in Section 2.3. The rate parameter a^{ox} is determined by the diffusive processes in the oxide film and the boron carbide itself. Therefore, it does not depend on the flow conditions and not on the steam partial pressure. In analogy to the oxidation of metals it can be surmised that the rate parameter a^{ox} goes to zero at very low values of the steam partial pressures.

In order to apply the newly developed model in simulations of tests done with boron carbide specimens, the computer code BORCA was developed. Some results of such code calculations will be discussed in the following. As a first point, results for the equilibrium film thickness as obtained for the correlations (10) and (11) are plotted in Fig. 1 versus temperature T (curve (1)). This means that in this way, the values have been obtained for the isothermal BOX tests under standard flow conditions. The values for curve (2) would be for tests in the BOX Rig with a steam partial pressure of 0.1 bar but with the same total flow rate as the tests of curve (1). It was assumed that the rate parameter b^{ox} depends linearly on the steam partial pressure (see Section 2.3 and Ref. [3]). Such tests have not yet been done, but would be very helpful.

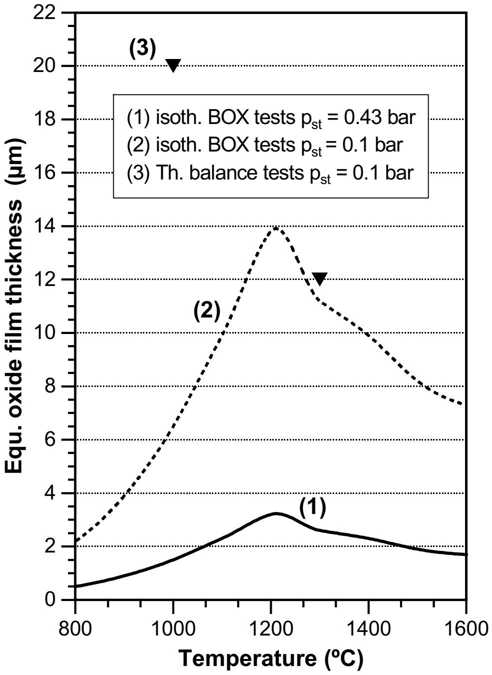

Fig. 1. Equilibrium values of oxide film thickness as a function of temperature.

There are indications from the literature [3] that under certain test conditions ($p_{\mathrm{st}} = 0.31$ bar) no oxide film is formed for temperatures below 600–700 °C. The authors concluded this from the fact that there was no net weight gain observed on the mass change curves and not by direct observation of the surface. It is difficult to judge the accuracy of the measurements. It could be that there is a formation of a very thin surface layer. This would then be qualitatively in accordance with the curve (1) for a high steam partial pressure and high flow rates.

Two values for tests done in the Thermo-Balance Rig [8] are also plotted in Fig. 1. In these tests the steam partial pressure was 0.1 bar but one had also lower total flow rates than in the BOX tests and therefore lower flow velocities. Only two calculated values exist and therefore a conclusion is difficult. It seems that a temperature dependence occurs, which differs from that in the BOX tests. The reason for this is not yet clear. But the values for the low steam partial pressure are roughly in the same range. Gravity effects are to be expected with oxide films in the range of 10–20 µm. No experimental data on oxide film thickness are known. However, there are observations on oxide film slumping effects in thermo-gravimetric tests [8] and observations from post-test examinations [7], which show thin surface layers. It should be noted that the authors in Ref. [3] found clear indications on the existence of an oxide film from mass increases in an initial stage for temperatures above 700 °C.

The calculated production rates of H_2, CO and CO_2 for a BOX test done at 1000 °C with a high density specimen are compared in Fig. 2 with measured ones. The calculated production rates reach their stationary values after about 50 s. The transient phase at the beginning is due to the build-up of the oxide film. The measured production of carbon oxides is in a first stage delayed and rises then distinctly above the level given by the stoichiometric reaction Eq. (1). This means that additional carbon is released which then reacts with steam to form carbon oxides. The same mechanism was also proposed in Ref. [3]. It was estimated for the test shown in Fig. 2 that about 1.5% of the carbon inventory of the boron carbide pellet was released that way. The slight increase of the hydrogen production rate is due to this effect. At the end of the test the increase comprises about 0.03 L/h. The initial transient phase in the calculated hydrogen production rate is much shorter than for the measured value. One problem concerns the initial conditions for the oxide mass m^{ox}. Of course, one cannot start with a value being zero. Also, in a very early phase the rate of oxide formation is determined by convective diffusion of steam towards the surface of the boron carbide pellet, if the surface is clean at the very beginning – another uncertainty about the initial conditions. This early stage of the oxidation process is indeed not simulated in the model.

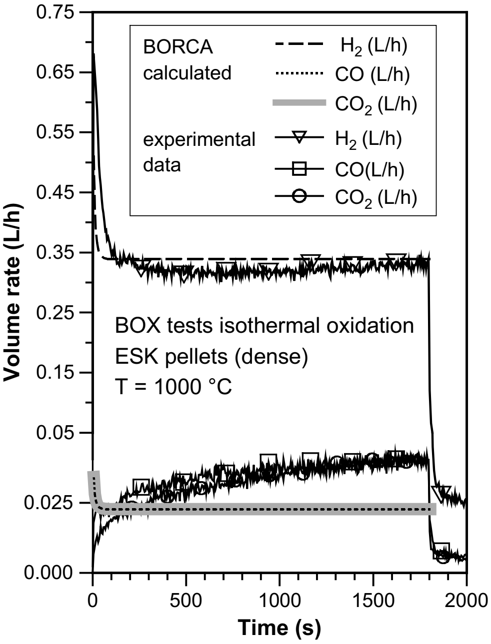

Fig. 2. Evolution of H_2, CO and CO_2 flow rates: comparison of measured and calculated values.

Fig. 3 shows a comparison of measured and calculated values of the total mass change on high density samples at the end of steady-state BOX tests. The agreement is very convincing. This gives us confidence that our simple empirical model allows to a large extent a satisfying simulation of the oxidation process and that the numerical values of the rate parameters are reasonable.

The model can be also applied to the tests done in the Thermo-Balance Rig [8], as can be taken from Fig. 4. In this case there was a transient phase in the temperature evolution followed by steady-state conditions. The calculated mass change curve does not perfectly match the measured one. This means that the model cannot simulate all the details of the experimental behavior. This is also known from tests in the BOX Rig (see Fig. 2). But on the whole the agreement is satisfactory, especially the duration of the first stage, where the mass increase due to oxide film formation is approximately balanced by the losses due to release of gaseous reaction products, is rather well reproduced. This gives us confidence that the calculated value for the equilibrium oxide film thickness of about 11 μm is more or less correct. Unfortunately, no measurements of the oxide film thickness were done. According to the lower steam partial pressure (0.1 bar), the lower flow rates and the different test set-up, the rate parameter b^{ox} had to be reduced with the help of a certain empirical factor f_b, taken to be constant. If one had allowed for a variation of this factor with the temperature T, a still better simulation

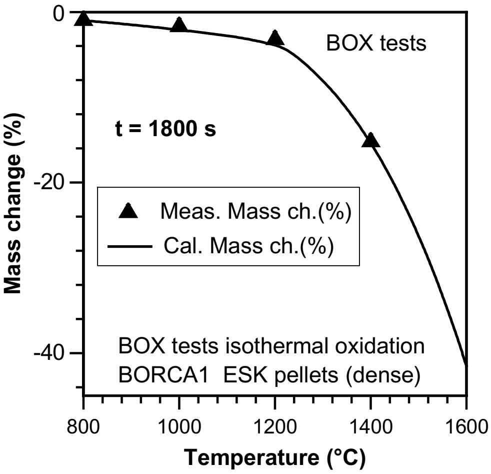

Fig. 3. Mass change of high density specimens: comparison of measured and calculated values.

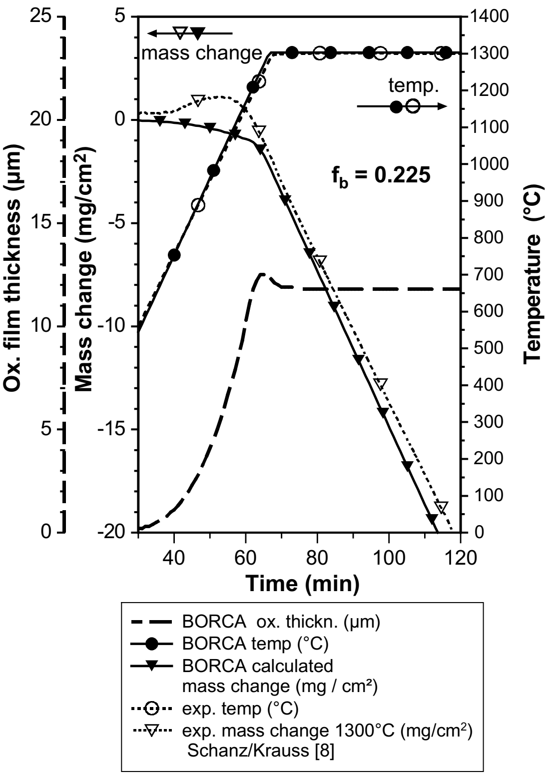

Fig. 4. Comparison of thermo-balance test with the BORCA model.

of the experimental results could be achieved. The factor f_b is determined by the ratio of the steam partial pressures and the ratio of the convective mass transfer coefficients relevant for the two flow configurations. This is discussed in Section 2.3.

2.2. Pore effect

The tests done in the BOX Rig [7] and in the thermobalance [8] have shown that porous material has for a certain time a much higher hydrogen production rate and a much higher mass increase rate than high density material. This is due to the contribution of the open porosity to the oxidation process. Steam diffuses through the system of open pores, and an oxide film of varying thickness is formed on the walls of the pore channels.

For the sake of simplicity the system of open pores is approximated by a certain number of pore channels opening up to the surface of the specimen. The main assumption of the pore model is that oxide film formation is determined by the steam supply through the pore channels.

The mass conservation law applied to an axial increment of the pore channel yields the following differential equation for the evolution of the oxide film thickness at an axial location x:

$$f_{\mathrm{ox}} \cdot A^{\mathrm{p}} \cdot D_{\mathrm{st}} \cdot \frac{\mathrm{d}^2 \cdot c_{\mathrm{st}}}{\mathrm{d}x^2} = f_{\mathrm{conv}} \cdot \rho^{\mathrm{ox}} \cdot U^{\mathrm{p}} \cdot \frac{\mathrm{d}\delta^{\mathrm{ox}}}{\mathrm{d}t}, \qquad (12)$$

where f_{ox} is the fraction of the steam flux consumed during oxidation, A^{p} the cross-section of the pore channels, D_{st} the steam diffusivity, c_{st} the steam concentration, f_{conv} the mass conversion factor, ρ^{ox} the density of the oxide film, U^{p} the circumference of the pore channel. It is assumed that the decrease of the steam density along the pore channel is proportional to a certain power of the density itself:

$$\frac{\mathrm{d}c_{\mathrm{st}}}{\mathrm{d}x} = -k \cdot c_{\mathrm{st}}^{n}. \qquad (13)$$

With this assumption the steam flux at the entrance of the pore channels j_{st} is determined by the rate constant k:

$$j_{\mathrm{st}}(T) = -A^{\mathrm{p}} \cdot D_{\mathrm{st}}(T) \cdot \frac{\mathrm{d}c_{\mathrm{st}}}{\mathrm{d}x}. \qquad (14)$$

This steam flux finally determines the whole mass change of the specimen due to the pore effect. As one does not know at the moment such fundamental physical properties like boric acid gas diffusivity and boric acid equilibrium gas pressure, one has implemented in the model an additional degree of freedom with the parameter f_{ox}.

The measured and calculated values of the hydrogen flow rate are given in Fig. 5 due to the pore effect alone together with values for the film thickness and the mass change for a test done in the BOX Rig with a low density pellet. The main tendencies of the experimental curve for the hydrogen production are to some extent met by the model, although the long persisting tail of the pore effect could not be reproduced. This effect could be due to some small fractions of large pore channels not yet included in the model. In order to be sure about the parameter f_{ox} experimental data would be needed on boric acid production for low density pellets.

2.3. Importance of the flow conditions

The oxidation rates measured so far by several authors [3–8] are all different. This is probably due to the different flow conditions, atmospheres and the variety of set-ups used in these tests, as the convective diffusion equation for the gaseous components depends on the whole flow velocity field. If experimental correlations for the Sherwood number or the convective mass transfer coefficient are available for a certain flow geometry, it is not necessary to solve the convective diffusion equation, but then one can have recourse to the following procedure. The convective mass flux in a fluid is given by the product of the mass transfer coefficient K and

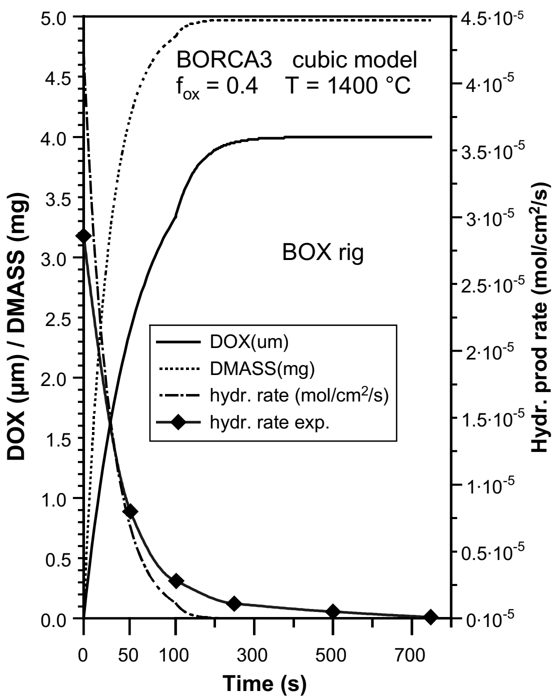

Fig. 5. Evolution of oxide film thickness, of the mass change and of the hydrogen production rate (pore effect).

the density difference between the bulk of the fluid and the surface of the specimen Δc. This is exemplified in the following for hydrogen, as in contrast to boric acid experimental data for this gaseous component are available:

$$j_{H_2} = K_{H_2} \cdot \Delta c_{H_2}, \tag{15}$$

$$\Delta c_{H_2} = c_{H_2}^{\mathrm{sur}} - c_{H_2}^{\mathrm{bulk}}, \tag{16}$$

$$Sh = \frac{K_{H_2} \cdot d_{\mathrm{hyd}}}{D_{H_2}} = \alpha \cdot Re^{\beta} \cdot Sc^{\gamma}, \tag{17}$$

$$Sc = \frac{\upsilon^{\mathrm{fl}}}{D_{H_2}}, \tag{18}$$

$$Re = \frac{u^{\mathrm{fl}} \cdot d_{\mathrm{hyd}}}{\upsilon^{\mathrm{fl}}}, \tag{19}$$

where Sh is the Sherwood number, Sc the Schmidt number, Re the Reynolds number, D_{H_2} the hydrogen diffusion coefficient, c_{H_2} the hydrogen concentration, K_{H_2} the hydrogen mass transfer coefficient, d_{hyd} the hydraulic diameter, υ^{fl} the kinematic viscosity of the fluid and u^{fl} the flow velocity.

It should be noted that the Reynolds number was in the order of 10 for the BOX and thermo-balance tests. That means, a laminar flow regime existed in both test series.

The viscosity of the fluid is calculated with the help of Wilke's method [11], as one has a multi-component gas mixture. The integral of the hydrogen flux over the surface area of the specimen interacting with steam gives then the hydrogen production rate. As one has no dependence on the axial position in the model (short length of the specimens), this would mean that one has to multiply the hydrogen flux with the active surface area of the specimen in order to obtain the total hydrogen production rate (see also Eq. (6)).

Eq. (13) is valid under the premises that there is no hydrogen production in the zone of convective mass transfer. According to Eq. (15) the convective mass transfer coefficient is determined by the correlation for the Sherwood number depending on the Reynolds and the Schmidt number specific to each flow configuration. In order to transform the oxidation rates from a certain flow configuration to a different one, one must know the respective correlations for the Sherwood number. This also determines the dependence of the rate parameter b^{ox} (see Eq. (6)) on the relevant flow parameters like system pressure, hydraulic diameter, flow velocity and steam partial pressure. In the BOX Rig the small B_4C cylinder is in a cross-flow position. As no correlations of the mass transfer coefficient for such a channel geometry could be found in the literature, use must be made of the analogy between heat and mass transfer. The premises for this are discussed in [12].

In [13] a correlation for the Nusselt number for long cylinders in rectangular channels are given as follows:

$$Nu = 0.3 + (Nu_{\mathrm{lam}}^2 + Nu_{\mathrm{turb}}^2)^{0.5}, \tag{20}$$

$$Nu_{\mathrm{lam}} = 0.664 \cdot Re^{0.5} \cdot Pr^{1/3}, \tag{21}$$

$$Nu_{\mathrm{turb}} = \frac{0.037 \cdot Re^{0.8} \cdot Pr}{1 + 2.443 \cdot Re^{-0.1} \cdot (Pr^{0.667} - 1)}. \tag{22}$$

This correlation should be multiplied with an empirical correction factor for short cylinders depending on the length to diameter ratio. Unfortunately, such a correction factor is not available. Also, the coolant channel in the BOX Rig was of a circular shape.

Making use of the analogy between heat and mass transfer, the Nusselt number has to be replaced by the Sherwood number and the Prandl number by the Schmidt number. The hydrogen concentration in the bulk of the fluid is certainly much smaller than that on the surface, as the specimens are of very short length (about 1 cm), one can calculate the hydrogen surface concentration from the hydrogen production rates measured in the BOX tests in equilibrium conditions. This parameter is viewed to depend only on the temperature and on the steam partial pressure, but it should be independent of the flow conditions. The author believes that the following representation should hold:

$$c_{\mathrm{H}_2}^{\mathrm{sur}}(T, p_{\mathrm{st}}) = p_{\mathrm{st}}^{\alpha} \cdot c_{\mathrm{T}}^{\mathrm{sur}}(T). \tag{23}$$

The data obtained from the oxidation tests in the BOX Rig suggest that the exponent of α is about 1. This is also suggested by the data correlation for the oxidation rate of [3]. The hydrogen flux in the BOX Rig depends on the steam partial pressure and under laminar flow conditions on the square root of the flow velocity u^{fl} (see Eq. (19)), which itself depends on the total flow rate. Thus, one gets the following dependence on these parameters in the BOX tests:

$$j_{\mathrm{H}_2} \propto p_{\mathrm{st}} \cdot \sqrt{\dot{m}_{\mathrm{st}} + \dot{m}_{\mathrm{Ar}}}, \tag{24}$$

where $\dot{m}_{\mathrm{st}}$ is the steam mass flow and $\dot{m}_{\mathrm{Ar}}$ is the argon mass flow.

Values of the hydrogen production rate for BOX tests done at 1200 °C versus the product of the steam partial pressure and the square root of the total mass flow (steam + Ar) are plotted in Fig. 6. Of course, there is some scatter in the data points. But on the whole the linear dependence is relatively well obeyed. That provides confidence in the model.

The hydrogen flux from the specimen to the fluid increases with the flow velocity. One could have even much higher transport rates with turbulent flow than under laminar flow. But this increase does not go beyond all limits. There are limits provided by either vaporization or by chemical reactions. These limits have not yet been determined experimentally. Therefore it is not clear, whether one would have indeed higher oxidation rates under turbulent flow conditions.

With tests done in an appropriate flow geometry one could determine the functional dependence of Eq. (23).

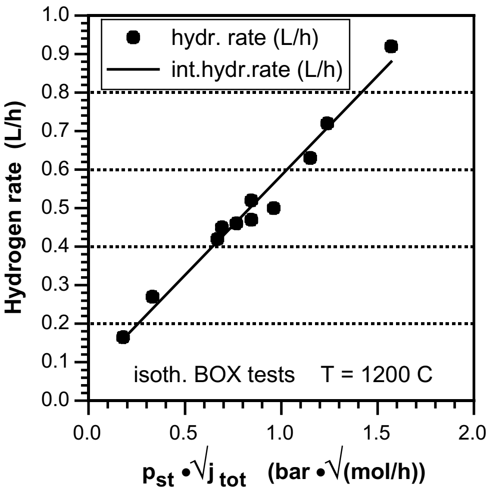

Fig. 6. Hydrogen rate as a function of flow parameter for cross-flow conditions.

For example, in fully developed convective mass transfer under laminar pipe flow conditions the Sherwood number is independent of the Reynolds number [14] and in this case one would have direct access to the hydrogen surface concentration.

The diffusion in multi-component gas mixtures can be described by the Stefan–Maxwell equation [15]. The solution of this equation would be rather demanding and has seldom been tried. If a dilute component i diffuses into a homogeneous gas mixture m, one can use Blanc's law [15]. According to this law, the diffusion coefficient of the component i in the mixture m is given by

$$D_{\mathrm{im}}^{-1} = \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{v_j}{D_{ij}}. \tag{25}$$

Neglecting the contribution of the carbon oxides and the boric acids Eq. (25) leads to the following equation:

$$D_{\mathrm{H}_2}(T) = (v_{\mathrm{st}}/D_{\mathrm{H}_2/\mathrm{st}} + v_{\mathrm{Ar}}/D_{\mathrm{H}_2/\mathrm{Ar}})^{-1}, \tag{26}$$

where $v_{\mathrm{st/Ar}}$ = steam/Ar mole fractions.

For the calculation of the binary diffusion coefficients the author has used the model of Fuller [16]:

$$D_{\mathrm{A/B}} = \frac{1.013 \cdot 10^{-7} \cdot T^{1.75} \cdot (1/M_{\mathrm{A}} + 1/M_{\mathrm{B}})^{1/2}}{p \cdot (V_{\mathrm{A}}^{1/3} + V_{\mathrm{B}}^{1/3})^2}, \tag{27}$$

where M is the molecular mass, V the molecular diffusion volume and p the total pressure.

One should note the dependence of the diffusion coefficient on the total pressure p that means the system pressure.

From the so-called oxidation rates of the BOX tests [7] the values for the hydrogen surface concentration obtained in the way described in the foregoing are seen in Fig. 7. The exponent α of the steam partial pressure in Eq. (23) has been set to 1. The following correlation fits the data quite well:

$$\begin{aligned} &\text{for } T \leqslant 1470\,\mathrm{K} : c_{\mathrm{T}}^{\mathrm{sur}} = 4.25 \cdot 10^{-6} \cdot \mathrm{e}^{-3.430/T}\ \mathrm{g/(cm^3\ bar)} \\ &\text{for } T > 1470\,\mathrm{K} : c_{\mathrm{T}}^{\mathrm{sur}} = 1.051 \cdot 10^{-2} \cdot \mathrm{e}^{-1.4900/T}\ \mathrm{g/(cm^3\ bar)} \end{aligned} \tag{28}$$

For the evaluation, a zero hydrogen concentration in the bulk of the fluid is assumed. This assumption is justified in view of the short length of the specimens (about 1 cm). For longer columns of B_4C the increase of the hydrogen bulk concentration with the axial position x must be taken into account. This is to be done with the help of the mass conservation law:

$$u^{\mathrm{fl}} \cdot \frac{\partial}{\partial x} c_{\mathrm{H}_2}^{\mathrm{bulk}} = \frac{U_{\mathrm{spec}} \cdot Sh \cdot D_{\mathrm{H}_2}}{d_{\mathrm{hyd}} \cdot A_{ch}} \cdot (c_{\mathrm{H}_2}^{\mathrm{sur}} - c_{\mathrm{H}_2}^{\mathrm{bulk}}), \tag{29}$$

where U_{spec} is the circumference of the B_4C specimen and A_{ch} the cross-section of the coolant channel.

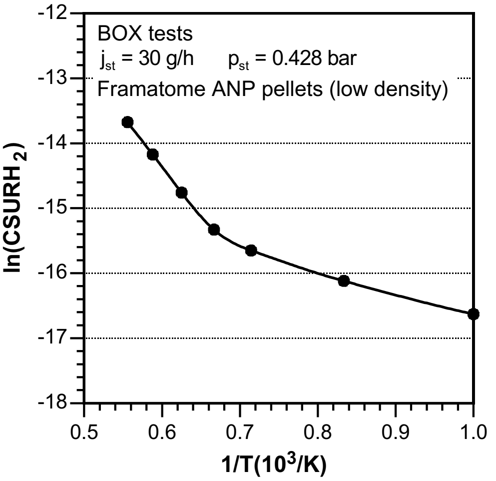

Fig. 7. Hydrogen surface concentration as a function of reciprocal temperature, obtained from the oxidation rates of the BOX tests.

Of course, there are considerable error margins in correlation (28), as the used correlation for the Sherwood number is not fully adequate for the test set-up in the BOX Rig, especially the specimen support in this rig had an influence, which cannot be quantified. But the author is rather confident that the postulated dependence on the square-root of the flow velocity and on the steam partial pressure is correct. Thus, only the pre-factor in Eq. (21) has to be modified to some extent. If one wants to calculate the oxidation of B_4C and the ensuing gas production in other environments than in the BOX Rig, as for example in an absorber element of a reactor under accident conditions, one must use Eqs. (15) and (29) together with Eqs. (3) and (6). It should also be kept in mind that the rate parameter a^{ox} does not depend on the flow conditions nor on the steam partial pressure. With the help of Eq. (9) the equilibrium oxide film thickness can then be determined. The lower the steam partial pressure and the lower the flow velocity, the higher will be the equilibrium oxide film thickness. But this scheme would be rather complicated. One can approximately estimate the transient phase with the help of a function $f(t)$, which describes the enhancement of the transient gas production rates, and multiply the hydrogen surface concentration with this function $f(t)$. The following expression reproduces the experimental data sufficiently well:

$$\begin{aligned} &t < t^{eq} : f(t) = \frac{1}{1 + (1 - 1/f_0) \cdot (t - t^{eq})/t^{eq}} \quad \text{with } f_0 > 1 \\ &t \geqslant t^{eq} : f(t) = 1 \end{aligned} \tag{30}$$

with f_0 the value of f at $t = 0$ and t^{eq} the time needed to reach equilibrium. This parameter depends slightly on the temperature and on the steam partial pressure. The following expression is proposed:

$$t^{eq} = 500 \cdot \frac{0.43}{p_{st}} \tag{31}$$

with t^{eq} in seconds and p_{st} in bar.

In this way one can calculate the hydrogen production rates with the help of Eqs. (15) and (29) and the other gas production rates and the mass change with the help of mass conversion factors. In the same manner one can also take into account the pore effect for low density boron carbide specimens with the help of an empirical factor in the hydrogen surface concentration.

3. Conclusion

The recently developed parametric model for the oxidation of boron carbide in steam gives on the whole encouraging simulations of tests with high density samples done in the BOX Rig [7] and in the Thermo-Balance Rig [8] at Forschungszentrum Karlsruhe, although not all the details of the tests are well reproduced. Some improvements could be achieved by modification of the chemical reaction equations, for example by the inclusion of an additional carbon release. The model predicts that an equilibrium oxide film thickness is reached, whose value is only determined by the two rate parameters of the model. An experimental determination of the oxide film thickness is still lacking and might also be somewhat problematic for high values of the steam partial pressure. Nevertheless, the author is quite confident that the main features, as the dependence on the temperature and on the steam partial pressure, are reasonable at least at temperatures above about 800 °C and steam partial pressures above about 0.1 bar.

Applying the principles of convective mass transfer in coolant channels enables to establish the link from the parametric model to a more generalized consideration. This allows to identify the hydrogen surface concentration as a parameter, which is independent of the flow conditions and presumably the test set-up. In that way one can extrapolate the experimental results of the BOX tests [7] to other experimental environments and other flow conditions.

The so-called oxidation rate of boron carbide is determined by the convective transport of the gaseous reaction products and depends therefore on the atmosphere and the flow conditions and of course on the experimental set-up. Under fully developed laminar pipe flow, for example, the Sherwood number would not depend on the flow velocity, but under turbulent flow conditions it would increase with a power of about 0.8. For the BOX Rig tests [7] and the TB Rig tests [8] one should have a square-root dependence on the total flow rate. Of course, the increase of the oxidation rate cannot go on indefinitely, but there should be an ultimate limit on the oxidation rate. This limit, which might be a function of the temperature and the steam partial pressure, has not yet been determined experimentally.

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