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Investigation of oxidation resistance of carbon based first-wall liner material Aerolor AO5

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Abstract

Minimizing the consequences of loss of vacuum and loss of coolant into vacuum accidents with respect to fusion reactor design requires the choice of materials as oxidation resistant as possible. In continuation to the testing of carbon candidate materials under oxidizing conditions (oxygen and steam) in collaboration with NET the carbon compound Aerolor AO5 of Carbone Lorraine has been examined in detail in the test facilities INDEX2 and SPALEX at Forschungszentrum Jülich. The parameters for these oxidation experiments in the in-pore diffusion controlled regime are temperature (from 973 up to 1173 K for oxygen, from 1173 up to 1423 K for steam) and reaction gas concentration (1–20 vol.% oxygen in argon, 5–100 vol.% steam in argon). The deducted equations for the primary oxidation reactions consider the dependence of the reaction rate on temperature, partial pressure and burn-off of the material. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In order to protect the metallic first wall of fusion reactors from direct interaction with the plasma an extra (carbon) armour is foreseen. Carbon offers the advantages of low atomic number, high melting point, high thermal conductivity and good mechanical stability up to high temperatures. Looking on the safety behaviour of fusion reactors it has to be noted that carbon is unstable against oxidizing media like oxygen and steam at high temperatures and has a high sorption capacity for tritium. Tritium, which is a β-emitting radiotoxic species, is used as intermediate fuel in the actual reactor concepts. Accidents like loss of vacuum (LOVA) will lead to an air ingress into the vacuum vessel, oxidation of the hot carbon and a partial mobilization of the sorbed tritium. In a similar manner loss of coolant into vacuum (LOCIV) will lead to a water/steam ingress into the vacuum vessel, also accompanied by carbon oxidation and tritium release. Also formation of burnable gases occur during these accidents (carbon monoxide in case of LOVA and hydrogen plus carbon monoxide in case of LOCIV).

Accident analyses require kinetic data of the chemical reactions involved. The experimental data used until now in LOVA and LOCIV investigations have the disadvantages that the experiments of [1,2] (fusion related materials) consider only the temperature dependence whereas the experiments of [3,4] consider the main dependences (temperature, partial pressure and burn-off) but deal with HTR-graphites. Furtheron, the pre-tests (supported by NET) for different carbon based plasma facing components presented in [5–7] provide only a non-sufficient data basis for evaluation of rate formula. For AO5 we will present the main dependencies of the reaction rate under in-pore diffusion control.

2. Oxidation reactions during LOVA and LOCIV

During LOVA and LOCIV the oxidation process between carbon and the entering gases is a sequence of a

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heterogeneous primary and several heterogenous and homogeneous secondary reactions.

For LOVA the exothermic primary reaction is $v_C C + v_{O_2} O_2 \rightarrow v_{CO} CO + v_{CO_2} CO_2$ with v_i as stoichiometric coefficient of gas *i*. The ratio of these coefficients is temperature dependent and can be calculated using the correlation of Arthur [8]. The most important secondary reactions are $C + CO_2 \leftrightarrow 2CO$ and $2CO + O_2 \rightarrow 2CO_2$.

During LOCIV the primary reaction is given by $C + H_2O \rightarrow CO + H_2$. This reaction is endothermic and followed by the secondary reactions $CO + H_2O \leftrightarrow CO_2 + H_2$ and $C + H_2 \leftrightarrow CH_4$.

The kinetic of the above mentioned homogeneous reactions can be described by using semi-empirical correlations (see [9,10]). For the four heterogeneous oxidation reactions it is necessary to perform experiments for each carbon material. Any heterogeneous oxidation is a combination of the chemical reaction and the two mass transfer steps diffusion to the material surface and in-pore diffusion inside the material [11].

In this paper the experimental data for the oxidation of a carbon candidate material for the first wall limiter, Aerolor AO5 (2D-C(arbon)F(ibre)C(compound) material), with oxygen and steam are presented. All experiments have been performed under in-pore diffusion controlled reaction conditions, because – in contrast to the boundary layer mass transfer controlled range – the rate is material dependent and – in contrast to chemical regime – the rate is relatively high. The temperature range of the experiments is between 973 and 1173 K for oxidation with oxygen and between 1173 and 1423 K for oxidation with steam.

3. Test facility INDEX2

The experimental investigations of the oxidation kinetics have been performed in the test facilities SPALEX [5] and INDEX2 in Jülich. INDEX2 is the abbreviation for *ind*uctively heated oxidation *ex*periment with a maximum operating temperature of 1473 K and a maximum operating pressure of 0.12 MPa (see Fig. 1). It consists of the four units test section, reaction gas supply, product gas system and cleaning gas system.

In the test section of INDEX2 a hollow cylindrical carbon specimen is inductively heated up to operation temperature. During the tests the reaction gas flows through the specimen in the test section and oxidation reactions occur between the gas and the inner surface of the material specimen. Product gases formed flow together with the non-oxidized part of the reaction gas to the product gas system. Argon is used as cleaning gas and flows all the time along the outer surface of the specimen.

The geometry of the specimens is: Outer diameter about 20 mm, inner diameter about 10 mm (±0.03), total length about 35 mm and length of the inner bore hole about 27 mm. That results in a reaction surface of about 850 mm^2, available for the oxidation process.

4. Test series and test performance

The main conditions of the test series are summarized in Table 1 for the oxidation with oxygen and in Table 2 for the oxidation with steam. All tests were performed at total system pressures of about 0.105 – 0.14 MPa. Each test series is a sequence of several measurements with a characteristic duration selected so, that the burn-off increase per measurement remains in a suitable range.

After preparation of the specimen (cleaning, inserting into the test section) and of the facility (heating up of the specimen, mixing of the reaction gas) each measurement starts by opening the valve of the reaction gas line. During the measurement the specimen temperature is controlled. By closing the reaction gas line valve the measurement stops. After cooling down the specimen is removed and weighted (±0.1 mg) for determining the burn-off (weight-loss due to oxidation related to the inner specimen surface).

5. Results

In Fig. 2 the experimental results for the oxidation of AO5 with oxygen are shown. The calculated reaction rate is plottet versus the burn-off. Additionally the measurement uncertainty is shown in Fig. 2. The formula for the reaction rate of the AO5 is

$$\frac{\dot{m}_C}{[\mathrm{kg/(m^2 s)}]} = 79400\ \exp\left(-\frac{26253}{T_C/[\mathrm{K}]}\right)\left(\frac{p_{o_2}}{[\mathrm{Pa}]}\right)^{0.671} f(m_C) \tag{1}$$

with $\dot{m}_C$ as the reaction rate of carbon in [kg/(m^2 s)], T_C the temperature of carbon in [K], p_{O_2} the partial pressure of oxygen in [Pa], m_C the actual burn-off of Aerolor AO5 in [kg/m^2]

$$f(m_C) = f_1(m_C) + (f_2(m_C) - f_1(m_C)) \times (p_{o_2}/[\mathrm{Pa}] - 1140)/19860 \tag{2}$$

and

$$f_1(m_C) = \exp(-0.39928/(0.20 + m_C/[\mathrm{kg/m^2}]))$$

and

$$f_2(m_C) = \exp(-0.83921/(0.35 + m_C/[\mathrm{kg/m^2}])).$$

Fig. 2 shows a strong increase of reaction rate with burn-off at low burn-off values, whereas at high burn-off the rate becomes nearly stable; this behavior can be explained by the fact, that effective diffusivity and chemical reactivity both increase at low burn-off, but at high burn-off only diffusivity increases but reactivity

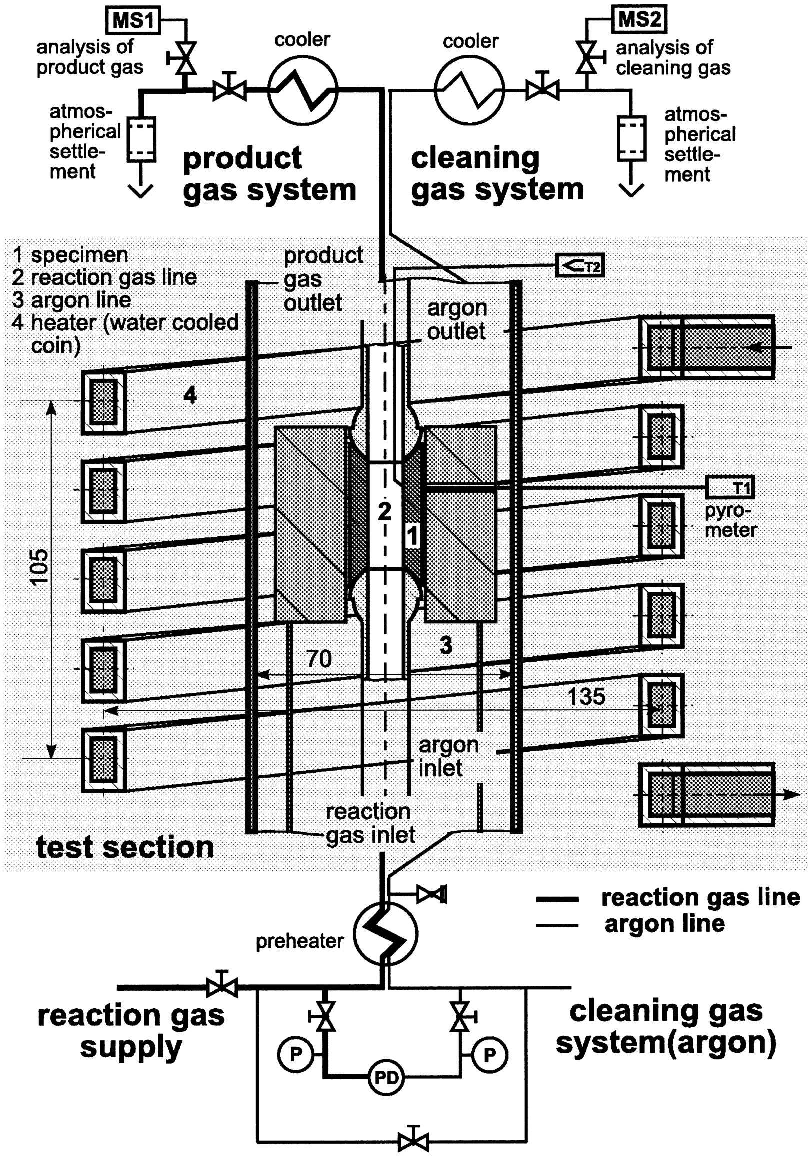

Fig. 1. INDEX2 test facility [5].

decreases with burn-off. As apparent activation energy a value of 218000 ± 11000 J/(mol K) is evaluated and the evaluation of the apparent reaction order gives a value of 0.671 ± 0.02.

The experimental results for the oxidation of AO5 with steam are presented in Fig. 3. The evaluation gives the following formula for the reaction rate of AO5 with steam

Table 1
Test series for oxidation with oxygen [5]

Measurement duration given in brackets		Reaction gas composition		
		1 vol.% O_2 and 99 vol.% Ar	5 vol.% O_2 and 95 vol.% Ar	20 vol.% O_2 and 80 vol.% Ar
	973		× (60 min)	
Temperature [K]	1073	× (30 min)	× (10 min)	× (3–5 min)
	1173		× (3 min)	

Table 2
Test series for oxidation with steam [5]

Measurement duration given in brackets		Reaction gas composition		
		10 vol.% H_2O and 90 vol.% Ar	50 vol.% H_2O and 50 vol.% Ar	100 vol.% H_2O
Temperature [K]	1173			× (180 min)
	1273	× (240 min)	× (60 min)	× (60 min)
	1423			× (10 min)

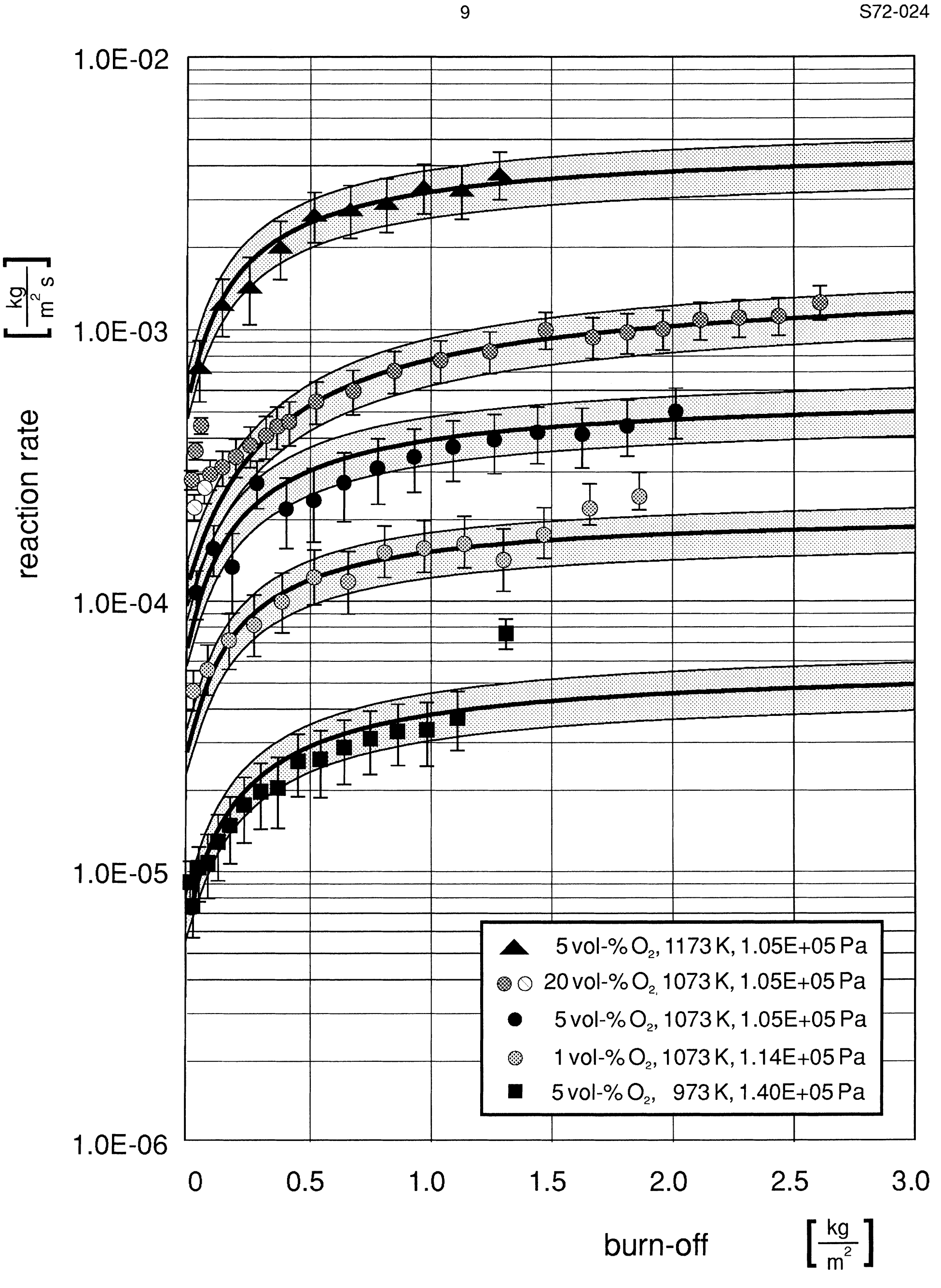

Fig. 2. Results of oxidation experiments of AO5 with oxygen [5].

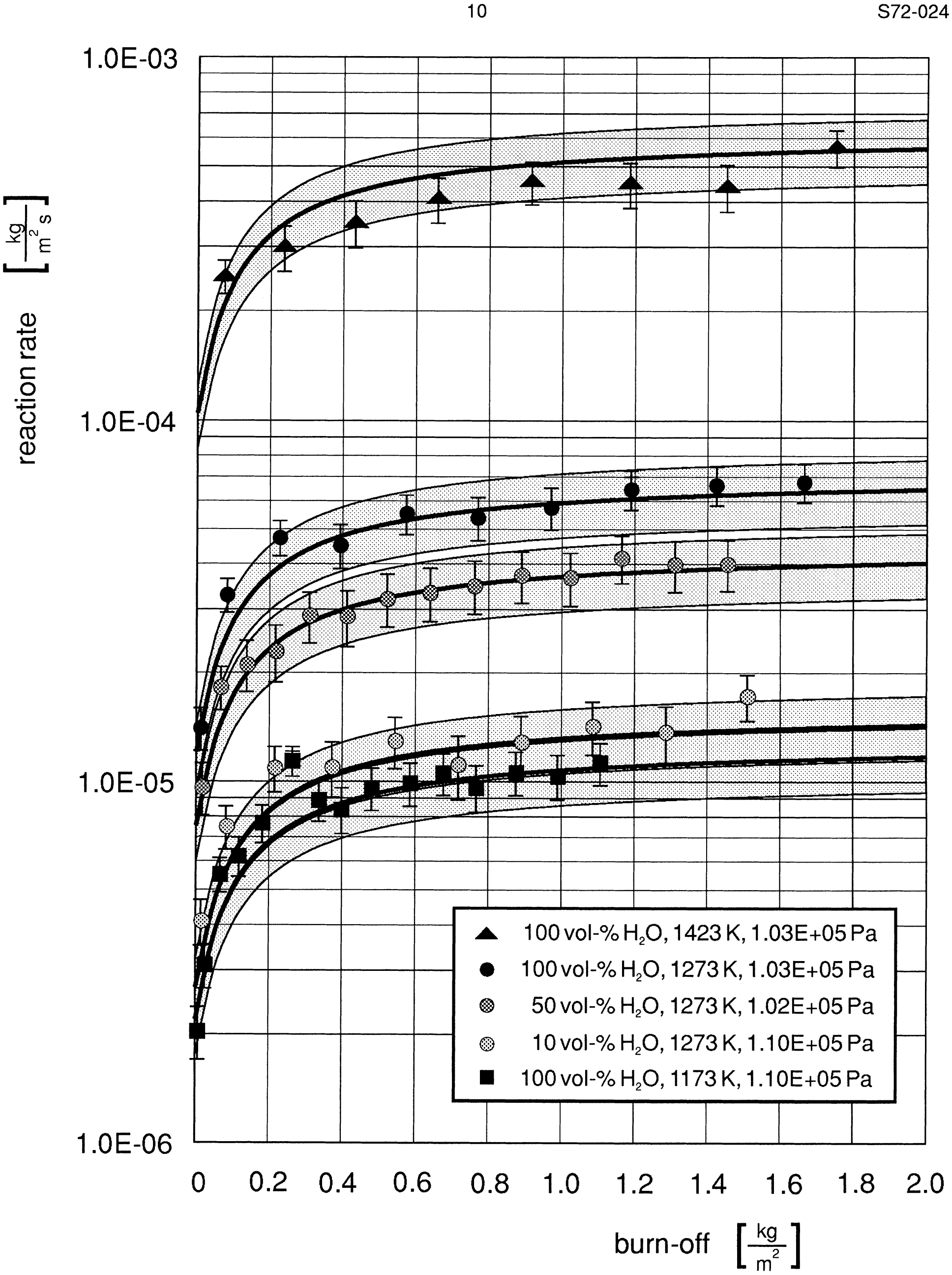

Fig. 3. Results of oxidation experiments of AO5 with steam [5].

$$\frac{\dot{m}_C}{[\mathrm{kg}/(\mathrm{m}^2\mathrm{s})]} = 24.80\ \exp\left(-\frac{26107}{T_C/[\mathrm{K}]}\right)\left(\frac{p_{\mathrm{H_2O}}}{[\mathrm{Pa}]}\right)^{0.671} f(m_C), \tag{3}$$

with the following burn-off dependence

$$f(m_C) = \exp(-0.202/(0.114 + m_C/[\mathrm{kg/m^2}])) \tag{4}$$

with an apparent activation energy of 217000 ± 11000 J/(mol K) and an apparent reaction order of 0.671 ± 0.006. In Eqs. (3) and (4) $\dot{m}_C$ is the reaction rate of carbon in [kg/(m^2 s)], T_C the temperature of carbon in [K], $p_{\mathrm{H_2O}}$ the partial pressure of steam in [Pa] and m_C the actual burn-off of Aerolor AO5 in [kg/m^2].

The Eqs. (1)–(4) should be used only with care at partial pressures outside the experimental range, because the apparent reaction order may be different. The extrapolation to other gas components and other total pressures is possible by multiplication of the above mentioned formulas 1 and 3 with the quotient of the diffusion coefficient of the oxygen (steam) at actual gas composition and pressure and the diffusion coefficient of the oxygen (steam) – argon mixtures at pressures as in our experiments. It should, however, be noted that such extrapolation is allowed only for the assumption, that Knudsen diffusion does not play an important role in gas transport within the pores, which is not yet validated for AO5.

The comparison of the above mentioned results of apparent activation energy with available experimental data for other carbon materials ([1–4,6,7]) reveals the following. The apparent activation energy of Aerolor AO5 for oxidation with oxygen is about 50% higher than the analogous value for the HTR-graphite V483T2 (131700 J/(mol K) [5]). The reason for this remarkable difference is not yet understood. Concerning rates that leads to reaction rates of AO5 higher than those of V483T2 at low temperatures. A comparison with the apparent activation energy for the graphite Union Carbide TS1792 and POCO AXF-5Q presented in [1] (47500 J/(mol K)) is uncertain because the majority of those experiments have been performed at higher temperatures where the material independent boundary layer diffusion dominates the overall oxidation rate. For the oxidation with steam a comparison of the apparent activation energy with HTR-graphites is presented in [12] which shows a good agreement (V483T2: 246000 J/(mol K), A3: 215000 J/(mol K)). For the oxidation with steam an apparent activation energy of 296000 J/(mol K) is presented in [2] for graphite GraphNOL N3M. This value is about 35% higher than the analogous value for AO5.

6. Oxidation model COX

Based on the experimental data for the in-pore diffusion controlled region of the primary reactions of the oxidation with oxygen and steam the kinetic computer model COX (Carbon Oxidation) has been evaluated [5]. The above developed rate formula together with literature formula for secondary reactions are implemented. Calculation of the heterogeneous reactions takes into account the mass transfer (boundary diffusion and in-pore diffusion) and the actual chemical reaction. This model and its implementation into the recently released version of the fluid dynamic code RALOC Mod 4.0 (*Ra*diolyse und *lo*kale Konzentrationen (der Gase) im *C*ontainment in Leichtwasserreaktoren) of the Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH [13] is described in detail in [5]. First calculations for LOVA in NET with leakage cross sections of 0.01, 0.1 and 1.0 m^2 and with different detailed nodalisation scheme of the fusion reactor (reaction chamber, plasma facing component first wall and divertor included inner cooling system) have been performed with COX-RALOC. The results of the rough nodalisation leads to burn-offs of 0.067 kg/m^2 (77 kg C for 0.01 m^2 leakage) to 0.121 kg/m^2 (140 kg C 1.0 m^2) with 168 kg (156 kg) carbon monoxide and 41 kg (57 kg) carbon dioxide formed. The comparison to earlier calculations of [14–17] shows that the more detailed consideration of the space dependent temperature, partial pressure and burn-off leads to much more detailed burn-off values of the carbon at the different regions inside the reaction chamber. Especially the results of the detailed nodalisation vary strongly with the circumference direction: All areas close to the leakage show high burn-offs up to 0.193 kg/m^2 (0.01 m^2 leak, 4 zone-nodalisation). Because with a 1-dimensional code it is nearly impossible to examine the expected location dependence, the application of a more-dimensional program is necessary. Therefore further calculations with the 3-D code CFX - after implementation of the model COX – are planned at Forschungszentrum Rossendorf for the next years.

7. Conclusion

For the first time detailed experimental data for the oxidation of a CFC material considering the main dependences of the reaction rate controlled by in-pore diffusion are provided. Further needs in this field are measurements to other reactions like Boudouard-reaction (secondary reaction) and generation of databases for other C-based candidate materials of fusion reactors (like Si-doped materials). In addition, special phenomena of fusion reactors like redeposited C-layers, should be examined with respect to their influence on oxidation behaviour. Also, the contribution of Knudsen diffusion in the in-pore diffusion process has to be known for extrapolation of data to other total pressures (as is necessary for steam ingress in ITER with pressures up to 0.5 MPa).

References

[1] M.H. O'Brien, B.J. Merrill, S.N. Ugaki, Combustion testing and thermal modeling of proposed CIT graphite tile materials, EG&G Idaho, EGG-FSP-8255, 1988.

[2] G.R. Smolik, B.J. Merrill, S.J. Piet, D.F. Holland, Evaluation of graphite/steam interactions for ITER EG&G Idaho, EGG-FSP 9154, 1990.

[3] R. Moormann, Untersuchungen zu Störfällen mit massivem Wassereinbruch am Beispiel des Kugelhaufenreaktors PNP-500, Jül-Spez-333, 1985.

[4] W. Katscher, R. Moormann, Graphite Corrosion under Severe HTR Accident Conditions Summary Report of IAEA Specialists Meeting on Graphite Component

Structural Design in JAERI Tokai, Japan (8–11.9.86), JAERI-M-86-192, 1987.

[5] A.-K. Krüssenberg, Experimentelle und analytische Untersuchungen zu Luft- und Wassereinbrüchen in das Vakuumgefäß eines Fusionsreaktors, Ph.D., Berichte des Forschungszentrums Jülich, Jül-3333, December 1996.

[6] R. Moormann, H.K. Hinssen, A.-K. Krüssenberg, B. Stauch, C.H. Wu, Journal of Nuclear Materials 212–215 (1994) 1178.

[7] H.-K. Hinssen, A.-K. Krüssenberg, R. Moormann, C.H. Wu, Studies on PFC Oxidation in LOCIV and LOVA Accidents, Proceedings of the 18th SOFT (Karlsruhe, 22.-26.8.94), pp. 1433–1436.

[8] J.R. Arthur, Reactions between carbon and oxygen, Transactions of the Faraday Society 47 (1951) 164–178.

[9] J.B. Howard, G.C. Williams, D.H. Fine, Kinetics of carbon monoxide oxidation in postflame gases, 14th Symposium (International) on Combustion, The Combustion Institute, 1973, pp. 975–986.

[10] W.M. Graven, F.J. Long, J. Am. Chem. Soc. 76 (1954) 6421.

[11] E. Fitzer, W. Fritz, Technische Chemie – Eine Einführung in die Chemische Reaktionstechnik, Springer, Berlin, 1975.

[12] A.-K. Krüssenberg, H.-K. Hinssen, R. Moormann, C.H. Wu, Experimental investigation of oxidation resistance of carbon based plasma facing materials of fusion reactors in steam, Proceedings of the European Carbon Conference Carbon 96, Newcastle, UK, 1996, pp. 104–105.

[13] B. Schwinges, W. Klein-Heßling, M. Heitsch, B. Hüttermann, Weiterentwicklung und Verifikation des Rechenprogramms RALOC, Abschlußbericht, GRS-A-2185, 1994.

[14] F. Andritsos, Y.G. Caouris, P. Rocco, M. Zucchetti, H.T. Klippel, E. Komen, J.P.A. van den Bogaard, T. Zylbersztejn, E. Drimille, F. Mazille, Loss-of-vacuum, loss-of-coolant and loss-of-flow accidents analyses for NET/ITER fusion technology 1990, Proceedings of the 16th Symposium on Fusion Technology (SOFT), vol. 2, 1991, pp. 1477–1481.

[15] H. Jahn, Final report on reactions of graphite with air, invessel combustion for the NET/ITER machine GRS-A-1713, 1990.

[16] P. Rocco, Y. Caouris, Loss-of-Vacuum Accidents (LOVAs) in NET/ITER – Final Report of the Sub-Task SEA 3-7 Technical Note No. I.91.144, ISEI/SER 2162/91, 1991.

[17] H. Jahn, Reaction of graphite with water/steam modelling of combustible gas production, distribution and consequence analysis, Final Report, GRS-A-1582, 1989.