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OXIDATION RESISTANCE OF CARBON BASED MATERIALS

by

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Dissemination level : CO
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Oxidation resistance of innovative C-based materials

1 Introduction

During the past 20 years a substantial number of new carbon materials was developed (particularly CFC and mixed materials), which show remarkable improvements with respect to certain properties like strength and thermal conductivity. The applicability of these innovative materials for HTRs was not completely checked up to now (because the innovative material development was outside the time range of main HTR R+D). Main aim of our work is a contribution to the question, wether these innovative materials are suitable for HTRs in the viewpoint of oxidation resistance. The materials considered here were partly developed for fusion applications (first wall etc.), but materials from other sources (like heat shields for rockets) are taken into account, too.

This report consists of:

- Oxidation measurements (oxygen/air and steam) in the chemical reaction controlled regime I and the in pore diffusion controlled regime II [1] in order to support promising developments in the area of innovative carbon materials, applicable in advanced energy technologies: As mentioned above, within the last twenty years, carbon fiber composites and mixed carbon materials (particularly those with Si) were developed, which show a substantial improvement of certain properties like strength and thermal conductivity. Such materials are already foreseen for fusion reactors, but may be also interesting for HTRs. Besides irradiation/strength measurements (done within another section of HTR-M) oxidation measurements are performed on selected innovative materials, i.e. 2D CFCs, 3D CFCs and mixed carbon materials with Si.

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CHEMICAL KINETIC DATA FOR ADVANCED OXIDATION MODELS

by

K. K uhn, H-K Hinssen, R. Moormann

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2 Experiments

Most of the experimental investigations were done in the THERA and the INDEX facilities. Experiments take place in the chemical reaction controlled regime I and in the in pore diffusion controlled regime II. The thermogravimetric apparatus THERA was used for the regime I. In regime II higher flow rates are necessary, which can be generated in the INDEX apparatus. Long-term experiments at low temperatures in air (673 and 773 K) were done in an annealing furnace.

2.1 The THERA facility

The THERA facility is an simultaneous thermal analyser where the experimental unit is coupled with the weighing system. So the weight loss of the investigated material can be measured directly during oxidation. The gas supply system in this facility is designed for reaction gas (which can be mixed with an additional gas via an second inlet) and inert gas. The exhaust unit can be coupled with a mass spectrometer or, in case of steam experiments, with an external weighing system to control the amount of H_2O which was injected during runtime.

The samples used in the THERA facility are small pieces of maximum 250 mg. The temperature, partial pressure and flow rate of reaction and inert gas is held constant during the experiments. The temperature of the samples is controlled over a thermocouple inside of the sample holder, which is situated beneath the sample. Measurements of the weight loss occur with an computerised program and can be observed over the whole runtime with an measuring interval of 20 s. A schematic presentation of the THERA facility is given in Fig. 2-1.

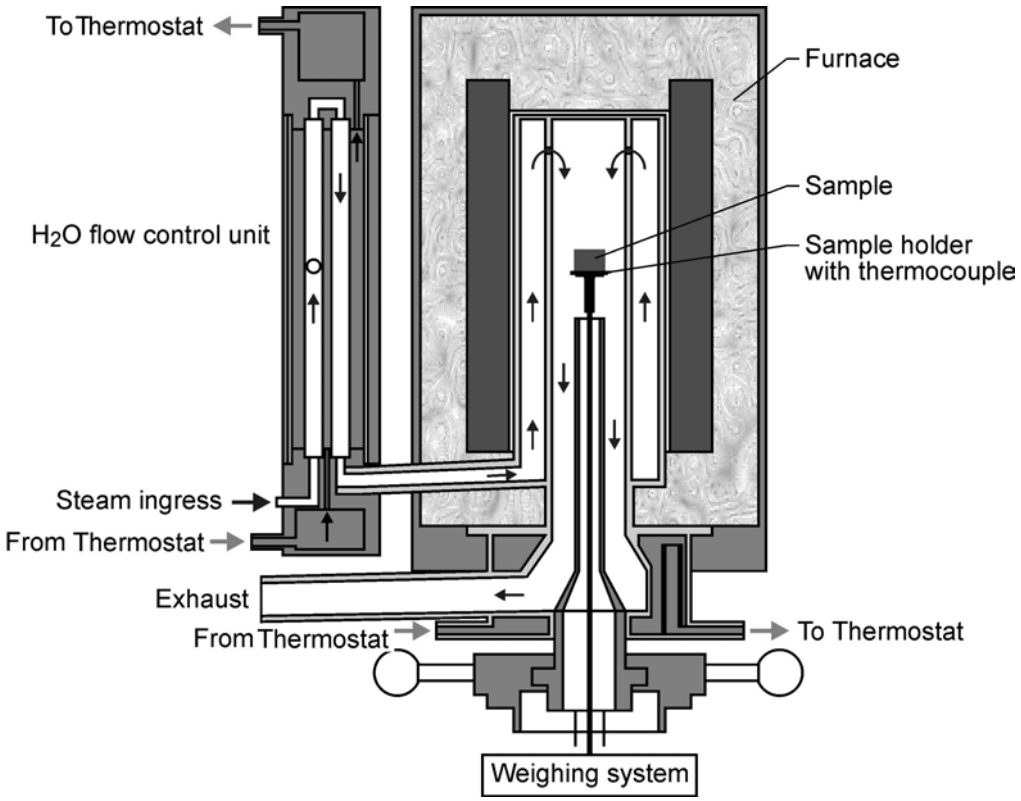

Fig. 2.1: Scheme of the experimental unit of the THERA facility

2.1 The INDEX facility

The INDEX facility is an inductive heated oxidation experiment, with a gas supply system for reaction gas, inert gas and product gas. In the sample cavity, a tube shaped graphite sample can be heated very fast over an inductive heating unit whereas the reaction gas flow through the sample. Thereby a oxidation reaction between the reaction gas and the inner borehole of the sample take place. During the experiment the outer region of the sample is rinsed with inert gas. Overpressure of the inert gas according to the reaction gas prevent the contact of the reaction gas with the outer surface of the sample. The reaction, inert and product gas, emitting at the exhaust can be measured by mass spectrometry.

The samples used in this facility have an outer diameter of 20 mm, an inner diameter of 10 mm and a total length of 30 mm. During the experiments temperature, composition and partial pressure of the reaction gas are constant. After a temperature- and reaction gas rate dependent duration of max 4 h, the supply of the reaction gas stopped and the sample cooled down and get weighed. The total weight loss is determined from the amount of the weight differences over the whole experiment in relation to the oxidation surface. A schematic presentation of the INDEX facility is given in Fig. 2-2.

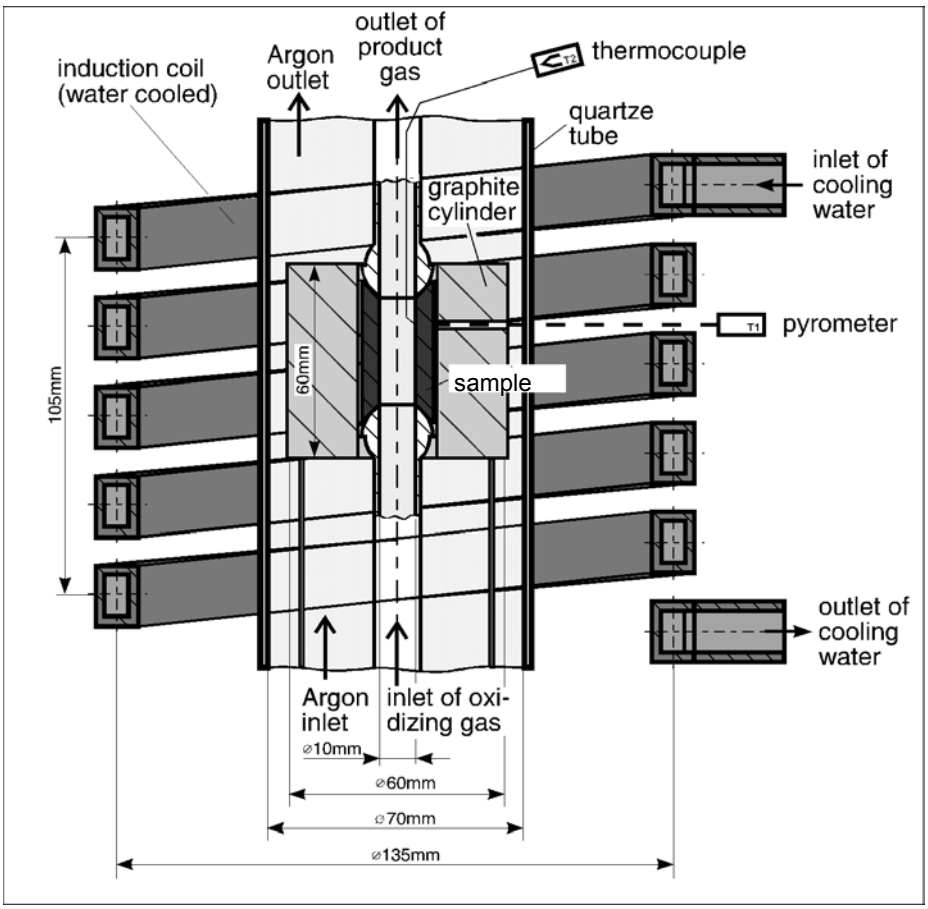

Fig. 2-2: Scheme of the central part of the oxidation facility INDEX

2.3 Investigated Materials

The different investigated materials are CFC-materials; some of the materials contain different amounts of silicon (3D-CFCs: NS31, INOX A14, NOVOLTEX). The doping of Si into the carbon implicates a higher density and a lower porosity and is agreed to increase the oxidation resistance of the material by formation of an SiO_2-layer impermeable for oxidants. Furthermore the CFCs has, according to the direction of the fibres, to be subdivided in two directional (2D-CFC) and three directional (3D-CFC) materials. The main data of the investigated materials, which are examined in this report, are given in Tab. 2-1.

Tab.: 2-1: Investigated materials

Material	Description	Density [kg/m^3]	Ash-content	Si-content [%]
AO5	2D-CFC	1870	<200 ppm	-
N31 /NB31	3D-CFC	1920	<0,1%	-
NS31	3D-CFC	2120	<0,1%	8-10
INOX A14	3D-CFC	2100	<0,1%	40
NOVOLTEX	3D- CFC	>2000	<0,1%	40

2.4 Experimental conditions

The experiments in regime I were performed under isothermal conditions at temperatures between 773 – 1073 K in air, and between 1173 – 1273 K in steam. Regime II measurements in steam are done at 1273 K, former regime II measurements in oxygen [2,3,4] not listed in this table, cover a temperature range of 923 – 1123 K. The partial pressures diversified between ambient pressure (annealing furnace), 1 bar in air and 1.05 / 1.1 bar in steam (THERA / INDEX). The reason for slightly overpressure in experiments in steam in the THERA and INDEX facilities is to inhibit air ingress from the exhaust into the cavity. The final weight losses diversified between ~ 60 and 100 % and the run times between 8 – 1300 h in air and between 10 – 45 h in steam. The experimental conditions are given in Tab.2-2.

Tab. 2-2: Experimental conditions

T [K]	Material	Reaction gas	Facility	P	Gas flow rate
773	N31 NS31	Air	Annealing furnace	1 atm	natural gas convection
833	NS31 AO5	Air	THERA	1 bar	12 [l/h]
873	AO5	Air	THERA	1 bar	12 [l/h]
923	NS31	Air	THERA	1 bar	12 [l/h]
1023	NS31 AO5	Air	THERA	1 bar	12 [l/h]
1173	NB31 NS31 AO5	Steam	THERA	1.05 bar	6-8 [l/h]
1253	NB31 NS31 AO5	Steam	THERA	1.05 bar	6-8 [l/h]
1273	INOX A14 NS31 NOVOLTEX	Steam	INDEX	1.1 bar	310 [l/h]

2.5 Results

Experiments in air

The experimental investigations in air show as expected a strong temperature dependence of the reaction rate. At low temperature (773 K) long-term experiments with a run time of 800 – 1300 h are necessary to reach burn off values above 50 %. At 773 K the Si-doped 3D-CFC material NS31 has less reactivity (about a factor of 2) in comparison to the undoped 3D-CFC N31. Both samples of the NS31 show nearly the same burn off values (Fig. 2-3), which gives an indication of the reproducibility of measurements.

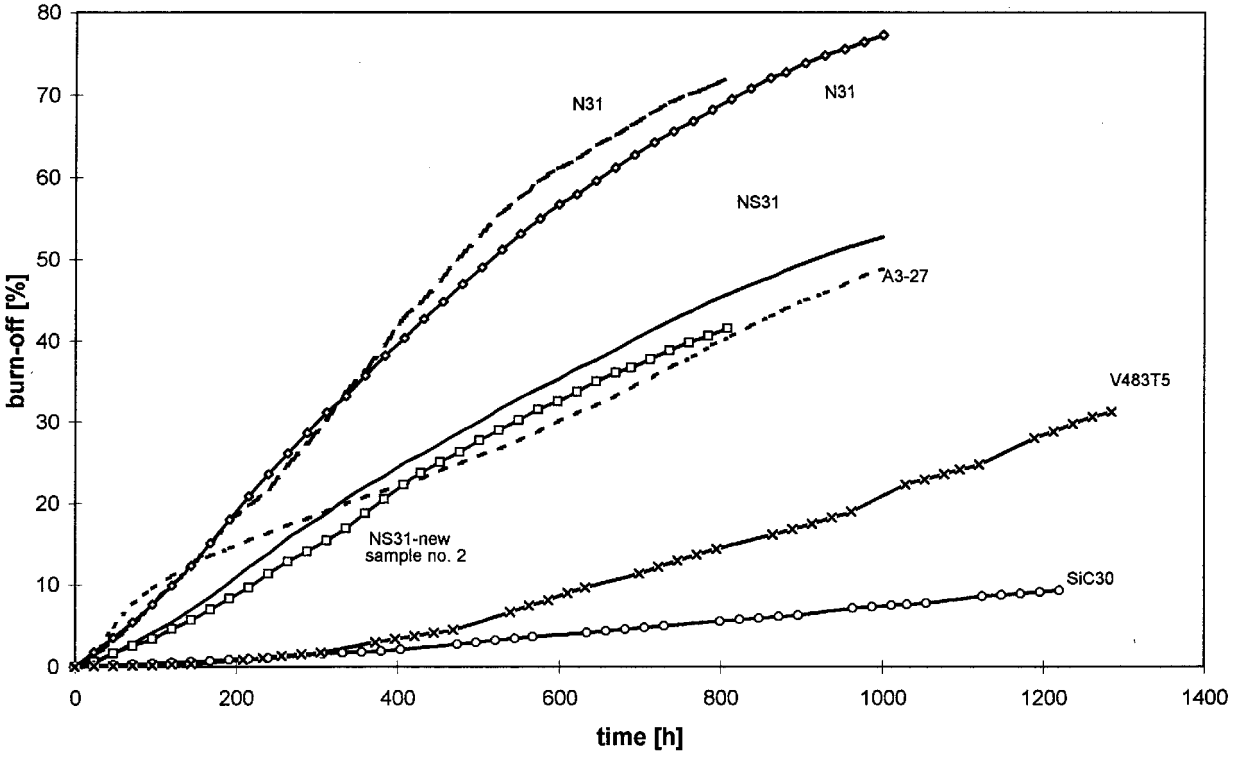

Fig. 2-3: Burn off versus time for different C-based materials in air at 773 K.

The CFC materials reveal rate increases with burn off (up to 30 % burn off) followed by a nearly linear decrease in regime I. An example for this behaviour is given in Fig. 2-4 for the 2D-CFC AO5. The rate increase of the AO5 is about a factor of 2.2 up to a maximum at 30 % and the activation energy is 150 kJ/mol at this maximum.

The formation of rate maxima can be explained by the kinetics of carbon oxidation. At low temperatures (regime I) the chemical reaction itself is the rate limiting step, the material oxidised homogeneously within the pore system. A strong burn off dependence of rate is due to the changing of the reactive surface during the oxidation process: Porosity increases by enlarging of the inner surface at low burn off, whereas at high burn off the pore walls vanish by oxidation and the reactive surface diminish. So the reactivity (inner surface) reaches a maximum at medium burn off values [1].

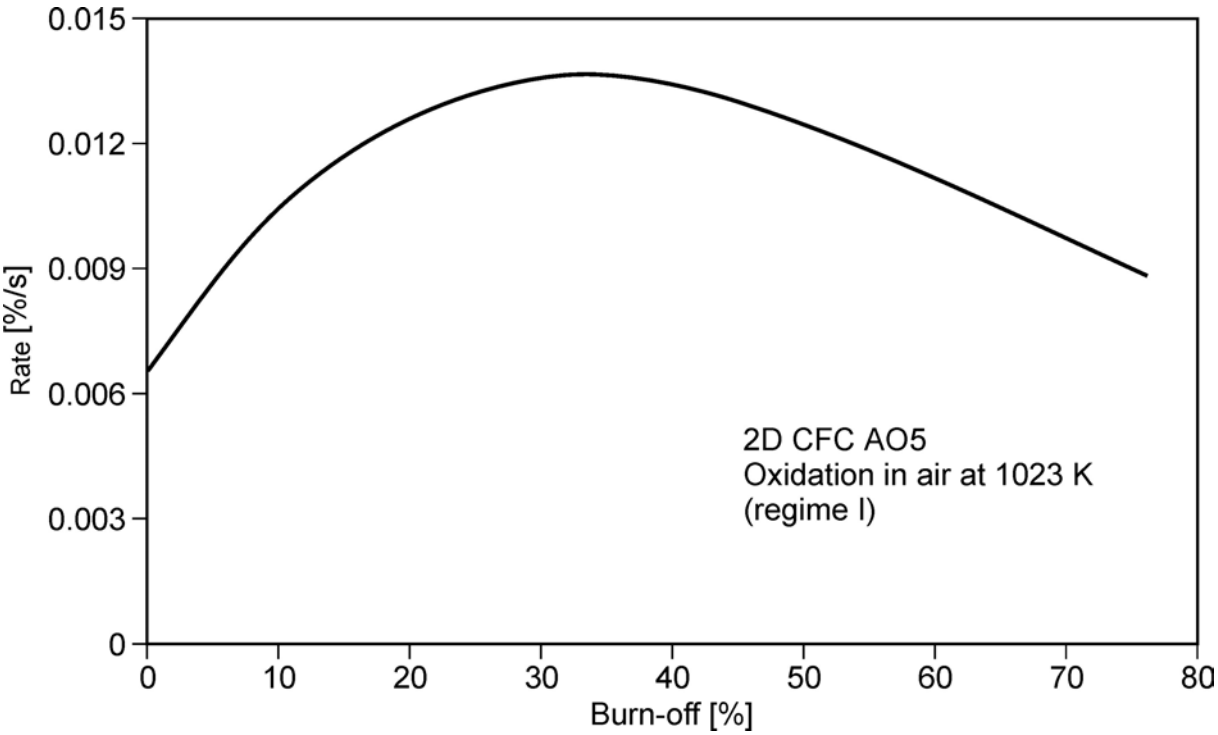

Fig. 2-4: AO5: burn off vs. rate at 1023 K.

In comparison the Si-doped 3D-CFC NS31 show a rate maximum at 15% burn off at 1023 K in the chemical reaction controlled regime I (Fig. 2-5). Here the weight change stems from the generation of solid SiO_2 and C-burn off. An activation energy of 175 kJ/mol was evaluated for the rate maximum. The oxidation rates of NS31 are not smaller than that of AO5 or the matrix graphite V483T, but a factor of 2 smaller than that of the undoped 3D-CFC N31.

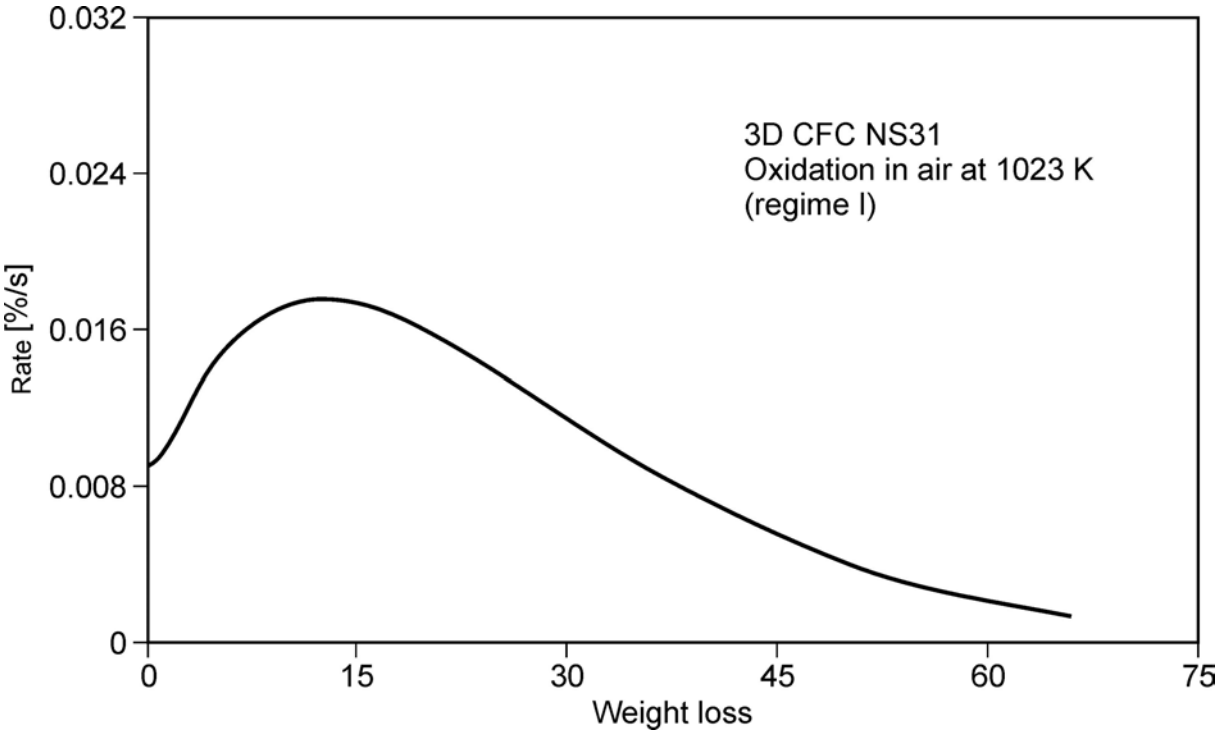

Fig. 2-5: NS31: weight loss versus rate at 1023 K

Experiments in steam

After steam oxidation in the chemical reaction controlled regime I (1173 and 1253 K) in the THERA facility a limited volume loss with a simultaneous higher porosity increase can be observed in all samples (Fig. 2-6). Accordingly the decrease of the size of each sample is relatively low, which is in line with the expectations for regime I. The 3D-CFC materials show oxidation along and inside of the single fibres without a breakdown of the structure. Contrary to that in the 2D-CFC AO5 the adjustment of the single fibres is not to be seen after oxidation. Here the morphology of the structure is achieved by ash particles whereas the carbon is oxidised. The observed strength loss after oxidation is in general very high, the 3D-CFC materials have the slightest strength loss after the experiments in regime I, probably due to preferential oxidation of matrix, whereas the fibre remain relatively unoxidised at oxidation start.

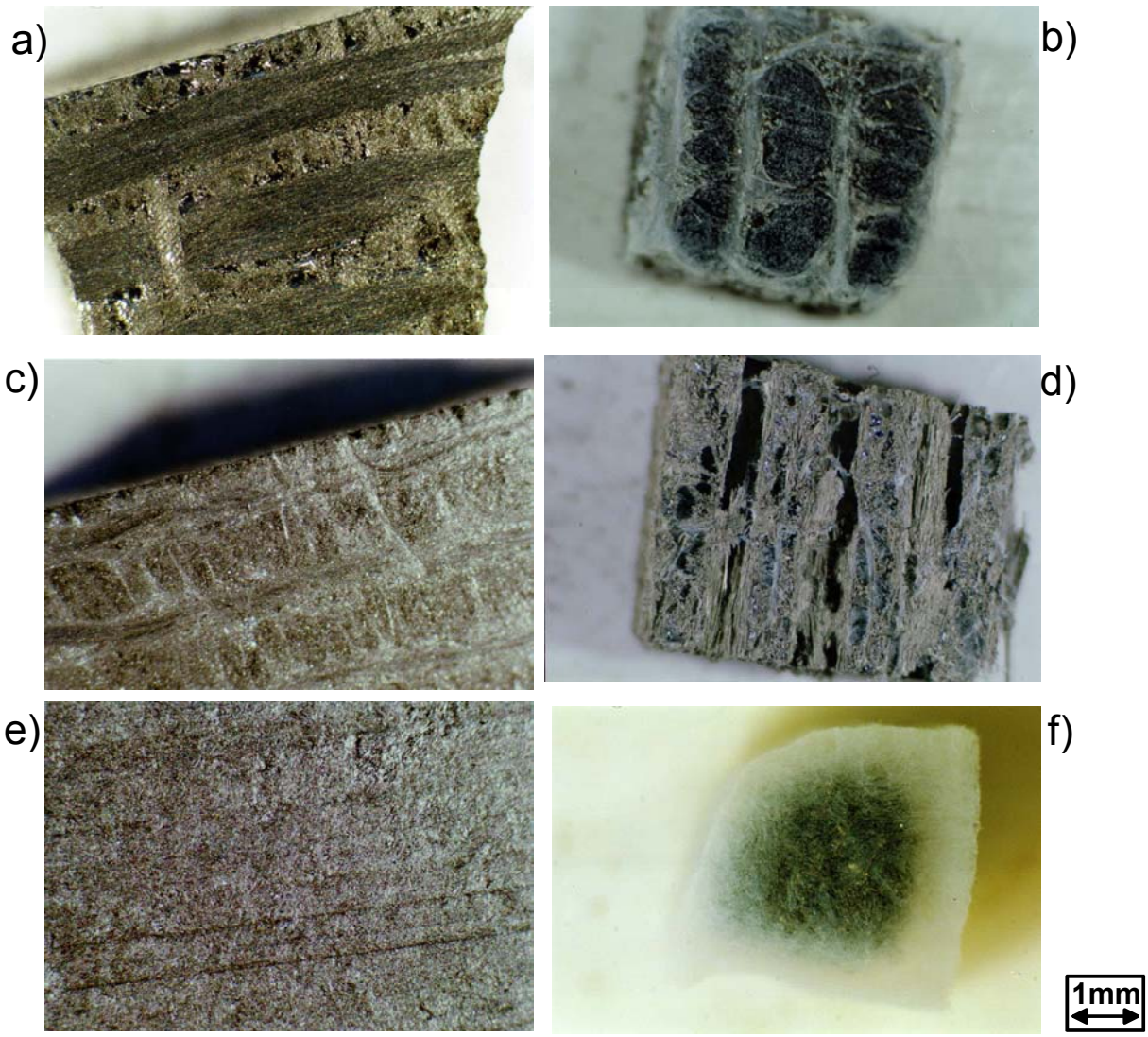

Fig. 2-6: Examples of investigated C-based materials. Left: unoxidised material; Right: samples after oxidation in steam. a), b) = NB31; c), d) = NS31; e),f) = AO5.

After oxidation in steam at 1173 K all samples were analysed with LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry, Elan 6000, Perkin Elmer; Sciex Corp., Norwalk, USA) in combination with a commercial laser ablation system (Cetac LSX 200, Cetac Technologies, Omaha, NE, USA) to represent ash analyses in relation to the impurity of the material. For the quantification of the analysed results a synthetic graphite-standard was used. The in Tab. 2-3 reported relative standard deviations (%RSD) is for several measurements (n = 3-6) at different sample areas. The higher the relative standard deviation the more the measurements differ. That means, that elements with a high deviation are inhomogeneous distributed in the sample. This was verified by the intensity of the matrix element ^{13}C which has a RSD of < 5%. Some of the analyses are semi quantitative and have a statistic error of 2-3 which is not significant in comparison to the quantitative results. The results of the trace element analyses is given in Tab. 2-3.

Tab. 2-3: Results of LA-ICP-MS analyses of different CFC materials.

AO5 Concentration [µg g^{-1}]				**NB31** Concentration [µg g^{-1}]				**NS31** Concentration [µg g^{-1}]			
Li	62[1]	Ba	338[1]	Li	0.7[4]	Ba	117[4]	Li	157[5]	Ba	437[2]
Mg	1860[1]	Ce	45[2]	Mg	8.3[5]	Ce	32[5]	Mg	2070[1]	Ce	52[2]
Al	225*	Pr	8.6[2]	Al	150*	Pr	4.1[1]	Al	152*	Pr	10.2[2]
Si	3250*	Nd	25[2]	Si	1085*	Nd	12.8[5]	Si	3780*	Nd	31[2]
K	-	Sm	4.9[2]	K	<10	Sm	2.6[3]	K	-	Sm	5.7[2]
Ca	21000*	Eu	1.4[1]	Ca	7260*	Eu	0.8[3]	Ca	-	Eu	1.7[2]
Ti	15000[5]	Gd	5.1[2]	Ti	175[4]	Gd	<1.0	Ti	8900[1]	Gd	6.3[2]
V	24[2]	Tb	0.55[2]	V	688[6]	Tb	<0.1	V	41[2]	Tb	0.73[2]
Cr	36[1]	Dy	3.7[1]	Cr	13.2[5]	Dy	<0.3	Cr	26[2]	Dy	4.4[2]
Fe	3200[1]	Ho	0.71[1]	Fe	94[5]	Ho	<0.06	Fe	3800[2]	Ho	0.87[3]
Co	11[5]	Er	2.0[1]	Co	1.3[5]	Er	<0.3	Co	12.8[3]	Er	2.3[3]
Ni	68[3]	Tm	0.27[2]	Ni	4.9[6]	Tm	<0.1	Ni	66[1]	Tm	0.28[3]
Cu	105[2]	Yb	1.6[1]	Cu	5.4[5]	Yb	0.7[3]	Cu	121[1]	Yb	2.0[2]
Rb	54*	Lu	0.24[1]	Rb	2.7*	Lu	<0.1	Rb	65*	Lu	0.28[2]
Sr	522*	W	5.5*	Sr	165*	W	184*	Sr	3700*	W	12.3*
Y	23*	Pt	15.4*	Y	2.0*	Pt	<0.2	Y	27*	Pt	114*
Mo	2.8[4]	Pb	387*	Mo	<0.7	Pb	1.1*	Mo	2.9[2]	Pb	891*
Sn	43*	Th	1.5*	Sn	3.2*	Th	0.5*	Sn	56*	Th	2.9*
Sb	4.9*	U	2.7[2]	Sb	<0.2	U	0.9[6]	Sb	6.3*	U	5.2[4]

[1] 10% RSD; [2] 20% RSD; [3] 30% RSD; [4] 40% RSD; [5] 50% RSD; * semi quantitative analyses
(Measurements conducted by Dr. C. Pickharts, ZCH-FZJ)

The results of the LA-ICP-MS analyses reveal clearly differences of the ash compositions of these materials: AO5 shows the highest contents of Ti, Ca, whereas NS31 has the most Mg, Fe, Si and Sr values but also very high Ti, Ni, Cu and Pb compared to the others. NB31 has maximum amounts of Ca, Si and V. In comparison to the others NB31 shows the lowest impurities. The AO5 is the sample with highest integral impurity content, which may explain the fact that the morphology of the sample is achieved by ash particles (see Fig. 2-6). In case of possible catalysis effects the Ti amounts are relatively high but other catalytic active elements like K and Rb show very low concentrations. So we can't exclude local catalysis, but at temperatures of 1173 K a reaction dominating effect by catalysis can be excluded.

Postexaminations of the Si-doped CFC INOX A14 after experiments in the in pore diffusion controlled regime II with REM was performed. Here white SiO_2 particles are visible on the outer surface after oxidation (Fig. 2-7) These SiO_2 particles were formed from SiC by oxidation.

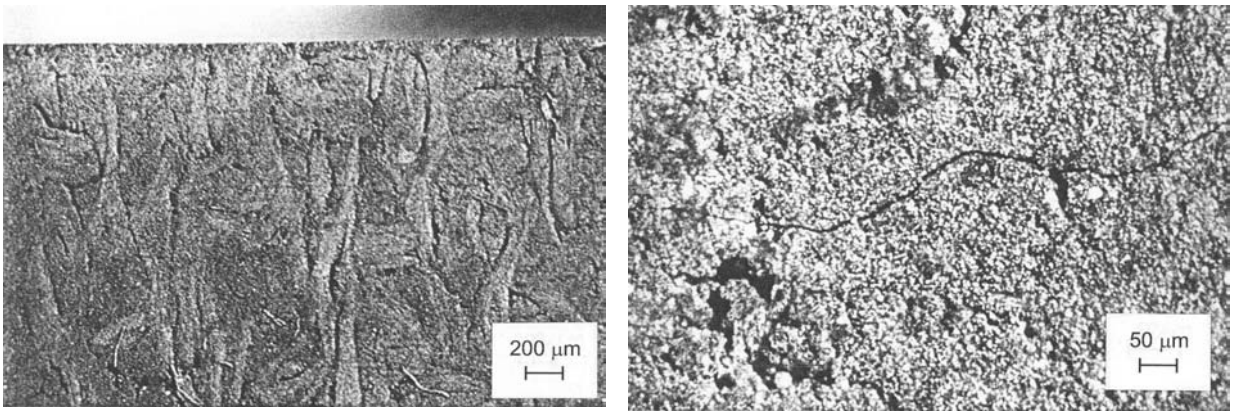

Fig. 2-7: REM of Si-doped 3D-CFC INOX A14 unoxidised (left) and after oxidation in steam at 1273 K (right).

The presentation of the results from experiments in the chemical reaction controlled regime are given in Fig. 2-8 to 2-12. Fig. 2-8 and 2-9 contain the burn off versus time curves for the materials and Fig. 2-10 to 2-12 the reaction rates versus burn off, which resulted from the burn off over time values.

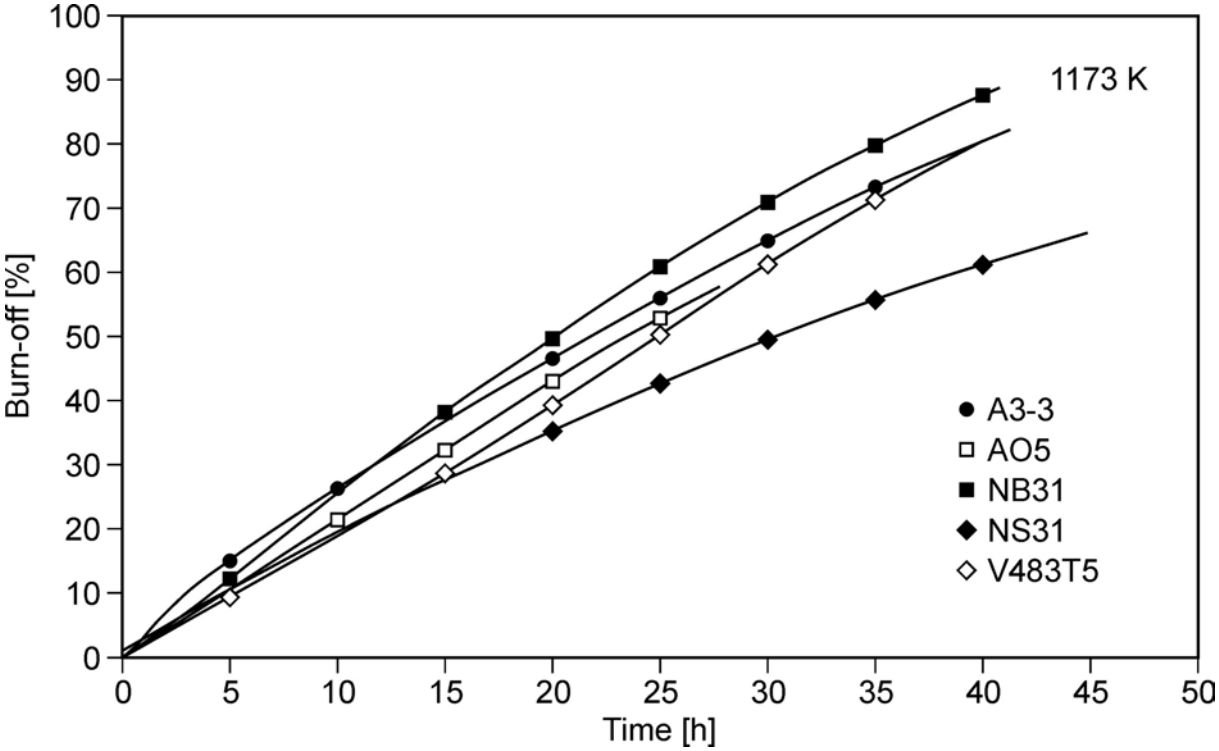

Fig. 2-8: Burn off vs. time for Oxidation in steam at 1173 K

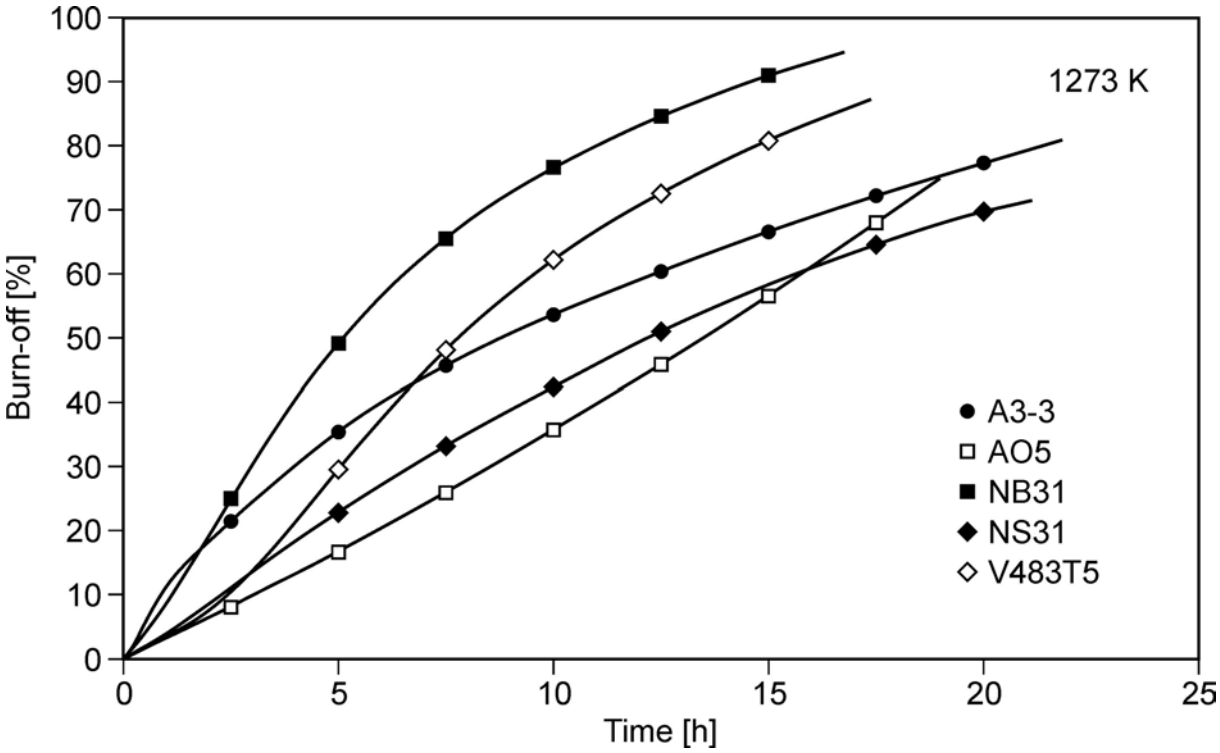

Fig. 2-9: Burn off vs. time for Oxidation in steam at 1253 K

It becomes obvious from these figures, that the reaction expired faster at higher temperatures (Fig. 2-8 and 2-9). The 3D-CFCs show roughly the samerelative oxidation versus burn off behaviour at both temperatures. The Si-doped NS31 has – as in air - burn off values about a factor 2 smaller than that of the undoped NB31.

The oxidation behaviour of AO5 show less pronounced maxima at 45 % burn off at 1173 K and 1253 K (Fig. 2-10). At low burn off values a slightly rate increase followed by a nearly linear gradient can be observed. The rate values are obviously smaller than that of the NB31 (Fig. 2-11).

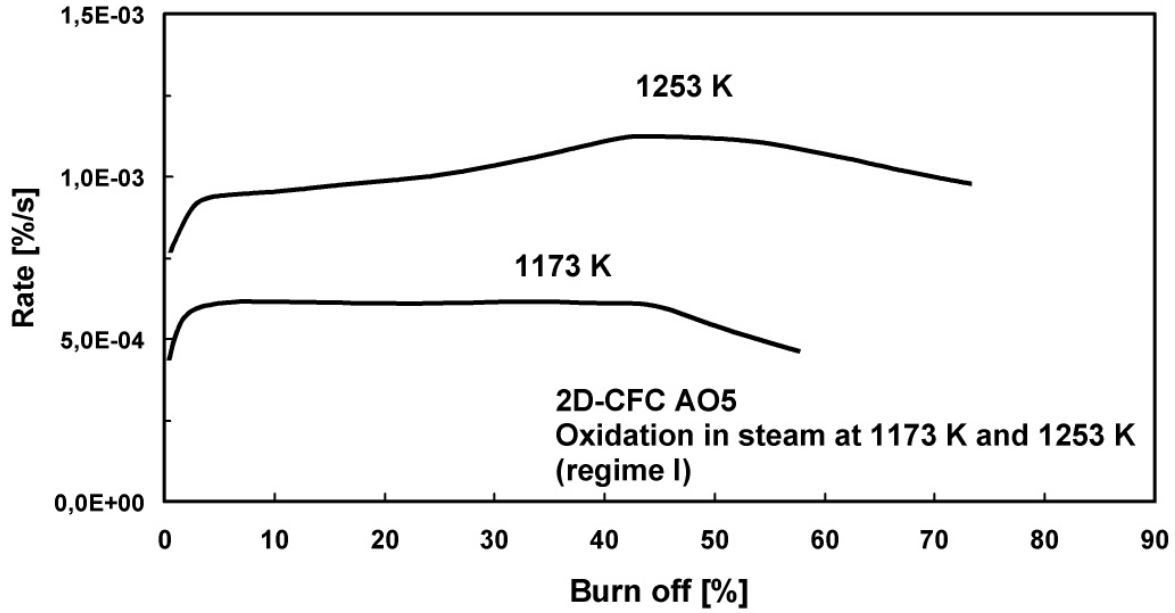

Fig. 2-10: AO5: Rate vs. burn off for oxidation in steam.

The undoped 3D-CFC NB31 shows a pronounced maximum at 20 % burn off for 1253 K (Fig. 2-11), whereas this maximum is less pronounced at 1173 K. The activation energy for maximum burn off is 216 kJ/mol.

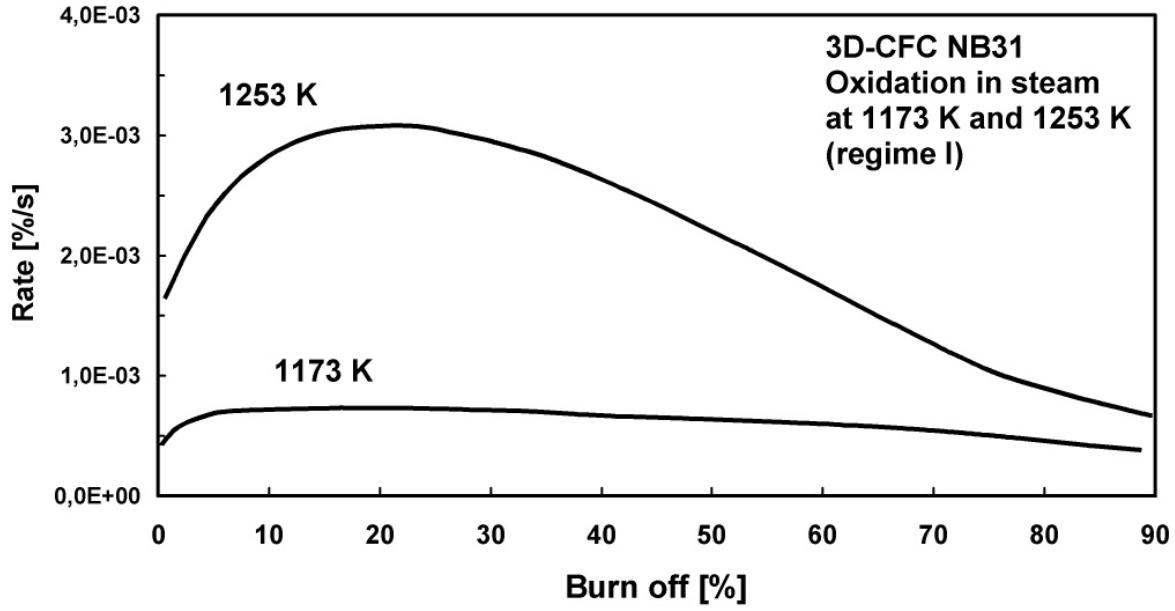

Fig. 2-11: NB31: Rate vs. burn off for oxidation in steam.

The oxidation behaviour of the 3D-CFC NS31 (Fig. 2-12) is, except by the rates being a factor of about 2 smaller, very similar to that of NB31. Also the maximum is less pronounced at 1253 K. The activation energy is only 141 kJ/ mol at peak maximum.

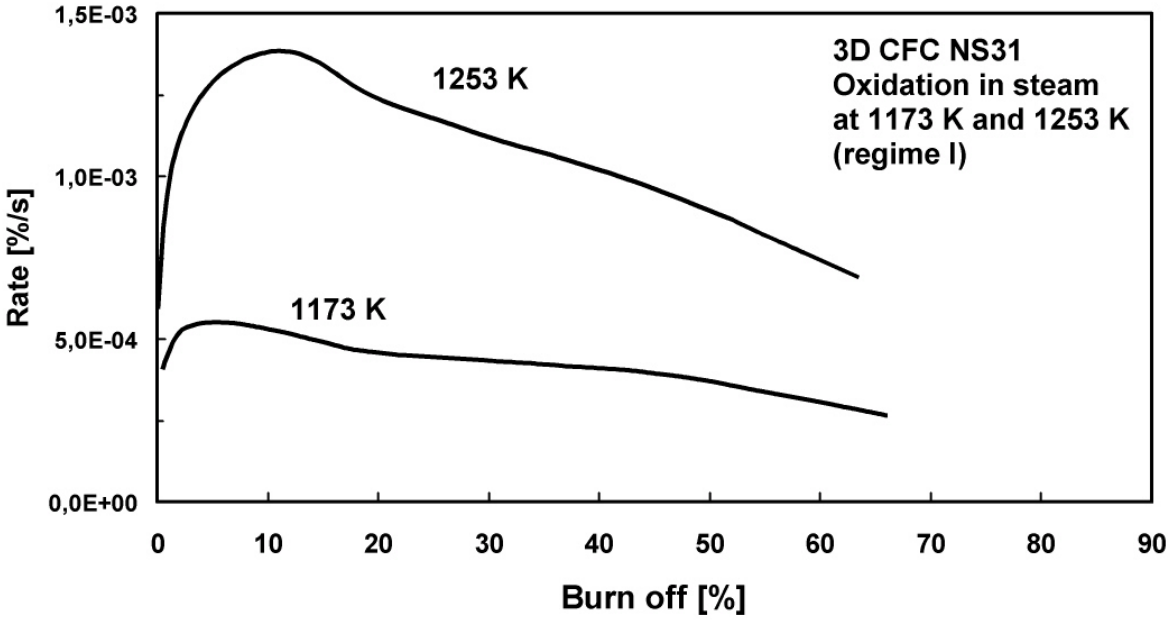

Fig. 2-12: NS31: Rate vs. burn off for oxidation in steam.

The results from experiments in the in pore diffusion controlled regime are given in Fig. 2-13. The shape of rate versus burn off curves in regime I is different from that in regime II where usually a plateau is formed. It should be noted, that the regime I/II transition does not only depend in temperature, but also on sample size: INDEX samples are of remarkably larger size than those of THERA; larger size decrease the transition temperature. Oxidation in regime II is usually accompanied by some mass loss by erosion, which is due to the high flow rates in combination with the oxidation induced strength loss. The gradient of the 3D-CFC INOX A14 point to a oxidation behaviour between regime I and II.

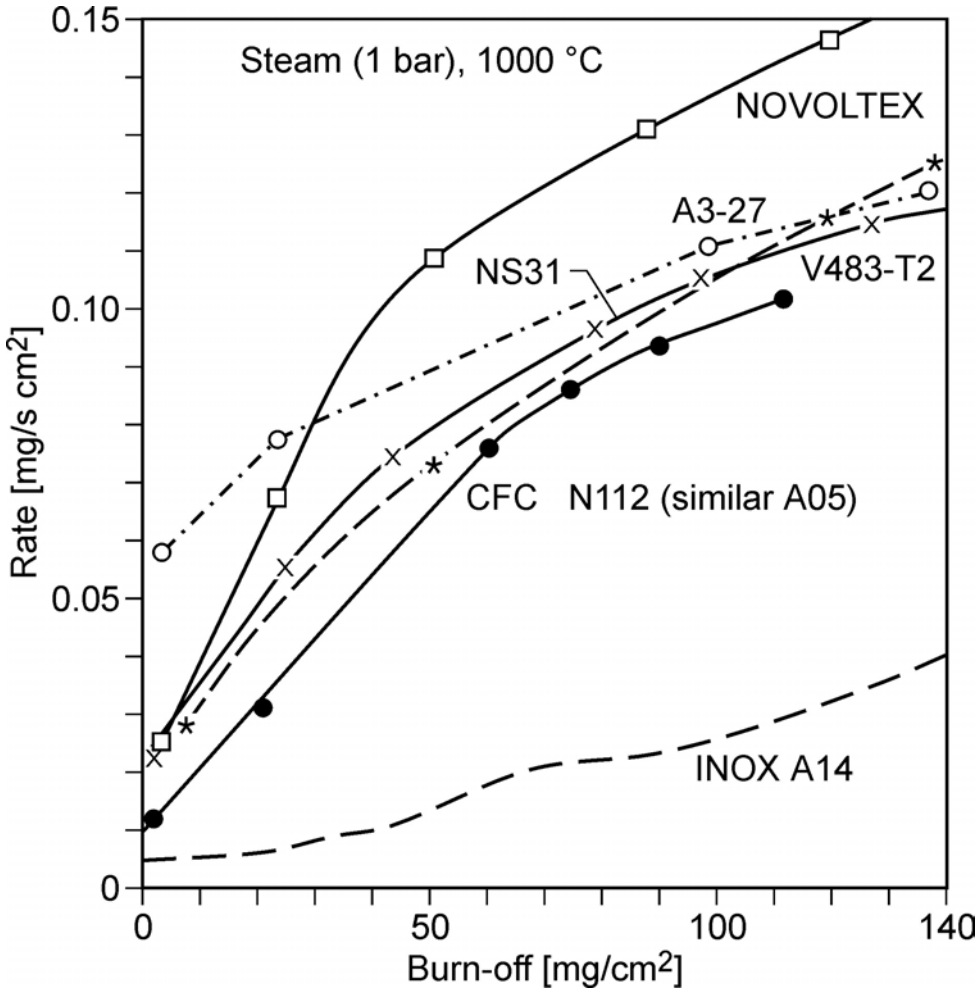

Fig. 2-13: Burn off versus rate for different C-Based materials in steam at 1273 K.

3 Oxidation resistance

3.1 Burn off dependent reactivities

As may be seen from figures 2-3 to 2-5 and 2-8 to 2-13, the general reactivity of these materials, which are listed in tab. 2-1, is not very different from that of normal graphites. There are some indications, that improvement of oxidation stability is still possible for some of these materials, i.e. an optimisation of oxidation resistance took not yet place. It was found out, that some of the innovative materials promise a better oxidation resistance in comparison to each other, but the spectrum of reactivities is almost the same than that of the normal graphites. So the Si-doped NS31 has a reactivity about a factor of 2 smaller than that of the undoped NB31, but not even better than that of the undoped AO5 or investigated nuclear graphites. A remarkable low reactivity in steam was found for INOX A14, which contains about 40% of Si; a material with similar Si-content (NOVOLTEX) did however not show this low reactivity. Rates of NOVOLTEX are by far too high (compared with all other materials and especially with INOX A14) which means, that this material is not yet optimised. [*1]

Concerning oxidation in air it has to be noted, that for low burn off values the lowest reactivity was found for the normal nuclear graphite V483T; its reactivity was even lower in that range than that of the SiC 30 material, containing 30 % of silicon. On the other hand the SiC 30 shows substantially improved oxidation resistance compared to the investigated CFC N31 without SiC (Fig. 2-3).

By postexaminations performed up to now we are not able to clarify the reason for this unexpected behaviour. These postexaminations however indicated, that in case of CFCs a preferential oxidation of the matrix occurred, whereas fibres were attacked in a later stage. In some cases, a change in reaction mechanism (porous matrix: in pore diffusion controlled regime = regime II; dense fibres: chemical reaction controlled regime = regime I) takes place after consumption of the matrix.

In case of the CFCs NB31, NS31 and AO5 the same differences in oxidation behaviour in air and in steam can be observed as for other advanced materials: Here the observed rate maxima, which were found in air are less pronounced in steam and so the exact shape of rate versus burn off curves is different in both gases. Furthermore the observed oxidation resistance in

steam at 1173 K correspond to those in air at 873 – 923 K, which is explainable by the endothermic character of the steam/carbon reaction.

[*1] A material similar to NS31, but with substantial higher heat treatment temperatures, is now offered by *Snecma Propulsion Solide*. It might be interesting to examine this material, too; this material is however very expensive.

References

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