1. Introduction

Carbon is added to the casting powder as a means to control its melting characteristics. Upon heating, the carbon is eliminated via the combustion reactions. The important phenomena occurring during heating of the casting powder are explained in Fig. 1. The temperature increases downwards in the flux layer. The powder added into the mold forms three main zones: a zone at the top consisting of loose powder, an intermediate sintered layer, and a liquid slag pool in contact with the steel. The combustion occurs in the loose powder zone and in the upper part of the sintered zone where the pores are still connected. The oxygen from the air enters at the surface of the packing and diffuses downwards. There is no combustion yet in the surface region because the temperature is too low (excluding formation of flames). Then, when the temperature is sufficiently high the combustion starts with formation of carbon dioxide. In the lower region where the temperature is high the carbon dioxide reacts with carbon to form carbon monoxide. The carbon monoxide diffuses upwards and reacts with counterdiffusing oxygen from the air, to form carbon dioxide. A mixture of carbon dioxide and carbon monoxide leaves the packing at the surface. Thus, the carbon combustion is complex and it is very important for the practical application that heating rate and reaction rates are in balance so that the carbon is removed from the powder on melting. Otherwise there will remain residual carbon in the liquid slag pool that can carburize the steel.

There are numerous laboratory studies of carbon combustion in casting powder. Thermo-gravimetric and differential thermal analysis have been applied. Small samples (mg scale) were used in heating experiments, or larger samples (g scale) were oxidized during holding at constant reaction temperature. In such experiments there is no temperature gradient within the powder. However, in real continuous casting conditions are more complicated because there is the temperature variation in the packing causing the internal combustion with several chemical reactions, depending on the local temperature, and diffusion of various gaseous species between the different temperature zones. It has been shown that in a temperature gradient car-

Fig. 1. Structure of casting flux layer in continuous casting mold with carbon combustion reactions. Schematic.
bon profiles can develop within the powder packing with a pronounced minimum and maximum.7)

The present work refers to the upper part of the casting flux layer in the mold where it is still in the form of loose or slightly sintered powder. The carbon combustion was investigated from a fundamental point of view. Carefully controlled experiments were carried out, simulating the thermal conditions in continuous casting, and a theoretical model was developed for the quantitative treatment of the internal combustion kinetics.

2. Experimental Investigation

2.1. Experimental Technique

Figure 2 shows a schematic sketch of the experimental apparatus. It consists of a vertical tube furnace, a clear quartz reaction tube containing the powder with flat bottom of 3.81 cm outside diameter, 2 mm wall thickness and 10 cm height, and a super alloy rod which is inserted into the furnace to move the hot zone to the upper part. The quartz crucible rests on the rod and extends outside of the furnace so that the bottom of the powder column attains a high temperature (up to 1000°C) and its upper surface a low temperature. In the experiment the furnace is heated to the desired temperature. Then the crucible, filled with powder to about 5 cm height, is placed on top of the super alloy rod. After the reaction time the crucible is removed from the rod and cooled to room temperature, and the carbon profile is determined.

In several experiments the top end of the crucible was open to the surrounding air, Fig. 2(a). But in part of the experiments it was intended to monitor the real time off-gas composition. For this purpose the quartz crucible is closed gas tight with a lid which has an inlet for air and an outlet for the off-gas, Fig. 2(b). The air is taken from a cylinder. The off-gas first flows through a filter. Then it is passed through an electronic flow meter to measure its volume rate, then to the analyzer and finally into a gas hood. The contents of carbon dioxide and carbon monoxide are measured with the non-dispersive infrared method. The oxygen content is determined with an oxygen galvanic emf sensor.

The casting powder used in the experiments is a premelted powder. Its analysis as provided by the manufacturer is 47 mass% SiO₂, 37 mass% CaO (total Ca as CaO), 0.3 mass% MgO, 4.5 mass% Al₂O₃, 0.08 mass% TiO₂, 0.15 mass% Fe₂O₃, 10 mass% Na₂O, 4.5 mass% F, 0.27 mass% K₂O. The premelted powder was selected because it contains no carbonate. Therefore no superimposed effects of the carbonate decomposition reaction occur during the combustion of carbon. Also emission of other volatiles is minimized due to the prior melting. The sample is prepared by mixing the casting powder with 5 mass% graphite powder (also obtained from powder manufacturer) in a mixing machine.

2.2. Experimental Results

Figure 3 is the photo of a crucible with casting powder after heating one-directionally for 4 h. The temperature at the bottom was about 880°C. There is a variation of carbon
content along the direction of heating as can be observed from the color, which changes from gray to white to dark gray and then to white again along the packing from the top to the bottom. This indicates that at the top of the packing (gray zone) the carbon content is high. In the middle part (white zone) almost all the carbon is combusted. Then there is an increase of carbon content (dark gray zone) and, finally, another combustion region exists at the bottom (white zone).

The carbon content along the powder packing was analyzed with two methods. In the first method the volume fraction of carbon is measured on the basis of the gray scale analysis by using the image analysis software NIH Image.\(^8\)

The color of the powder at the top of the packing where no combustion took place is taken as a reference standard (carbon content of 5 mass% = volume fraction of 0.0141).

Then by comparing the gray scale along the powder packing, the carbon profile as shown in Fig. 4 was obtained. This method is comparatively fast and allows a direct comparison to the modeling result.

In the second method the mass fraction of carbon is determined by thermo-gravimetric analysis. The powder is taken out from the reaction tube layerwise, approximately 1 g per layer. Then each layer is heated in air at 800°C for 40 min in a platinum crucible to combust the remaining carbon, and from the weight change the average carbon content of the layer is obtained. The result is shown in Fig. 5.

Although the profiles obtained with the two methods have similar form, there is the feature that with the optical method the maximum (3) at the bottom is higher than the maximum (1) at the top, and with the gravimetric method the opposite is observed. This difference is caused by the density variation along the column. Mass fraction \(\gamma_C\) and volume fraction \(\varepsilon_C\) of carbon are related to each other by the formula

\[
\varepsilon_C = \frac{\gamma_C \rho_{\text{app}}}{\rho_C} \quad \text{..................................(1)}
\]

Hence, the increase of density (decrease of void fraction) in downward direction causes an increase of volume fraction of carbon compared to mass fraction. If the \(\gamma_C\) values are converted to \(\varepsilon_C\) values using the density–temperature function of the powder (Appendix), \(\rho_C = 2.2 \text{ g cm}^{-3}\) and the computed temperature profile (see next section) the \(\varepsilon_C\) profile in Fig. 5 is obtained with a higher bottom maximum, as in Fig. 4.

From the examination of the samples after the experiment it was evident that there were no voids or cracks in the packing, and no noticeable gap between powder and crucible. Shrinkage had occurred uniformly and solely in height direction.\(^*\) A radial change of color (carbon content) could neither be observed. Hence, it can be concluded that the combustion reactions and diffusion phenomena occurred uniformly over the cross section of the packing in the crucible and the resulting longitudinal carbon profile had essentially no radial variation.

3. Theoretical Model

Also the theoretical model applies to the upper part of the casting flux layer in the mold where it is still in the form of loose or slightly sintered powder, Fig. 1, and it is used in the following to simulate the combustion phenomena in the laboratory experiments. It is assumed, in accordance with the conditions in the experiments, that the void fraction of the powder is uniform over the cross section of the packing (no channels with flames), that the heat flow and mass transport are one-dimensional, that the only reactions are

\(^*\) This is not so with all powders. For instance, a powder mixture with 5 mass% carbon black exhibited also radial shrinkage and could not be used, therefore, for the present research.
The velocities of the oxide and the carbon are set equal, and the apparent density is assumed to follow the relation given by Russell. The longitudinal coordinate is denoted by z and has its origin at the bottom of the powder column (bottom of crucible). Hence, the temperature is highest at z=0 and decreases upwards. The upper surface of the column is at z=H(t) and is exposed to air.

The basic governing equations of the system along with their initial and boundary conditions are as follows. The list of the symbols is given at the end of the paper.

### 3.1. Heat Flow Equation

The heat flow equation used has the form

\[
\frac{\partial \rho H}{\partial t} + \frac{\partial \rho H v_c}{\partial z} = \frac{\partial}{\partial z} \left( \lambda_{\text{eff}} \frac{\partial T}{\partial z} \right)
\]

where

\[
\rho H = \rho_{\text{app}} H_{\text{app}} + \rho C_{\text{app}} H_{\text{app}} + \rho g C_{\text{app}} H_{\text{app}}
\]

The velocities of the oxide and the carbon are set equal, \( v_c = v_{\text{ox}} \). The effective thermal conductivity of the casting powder is assumed to follow the relation given by Russell:

\[
\lambda_{\text{eff}} = \left( \frac{1 - g_{\text{gas}}^{1/3}}{\lambda_{\text{solid}}} + \frac{g_{\text{gas}}^{1/3}}{(1 - g_{\text{gas}}^{1/3}) \lambda_{\text{solid}} + g_{\text{gas}}^{1/3} \lambda_{\text{gas}}} \right)^{-1}
\]

where \( \lambda_{\text{gas}} \) is obtained from the kinetic theory of gases and \( \lambda_{\text{solid}} \) is taken to be 2 W m\(^{-1}\) K\(^{-1}\).

### 3.2. Conservation Equations for the Gaseous Species

The conservation equations for carbon dioxide, carbon monoxide, molecular oxygen and atomic oxygen contain, in addition to the usual terms, the source terms which are composed from the rate constants of the chemical reactions involved. Neglecting thermal diffusion and using an effective binary diffusion coefficient in the ordinary diffusion fluxes yield the following expressions:

\[
\frac{\partial g_{\text{CO}_2}}{\partial t} + \frac{\partial g_{\text{CO}_2} v_{\text{gs}}^*}{\partial z} = \frac{\partial}{\partial z} \left( D_{\text{eff}} \frac{\partial g_{\text{CO}_2}}{\partial z} \right) + \eta_{\text{CO}_2} - \eta_{\text{CO}} + \eta_{\text{CO}}
\]

and

\[
\frac{\partial g_{\text{CO}}}{\partial t} + \frac{\partial g_{\text{CO}} v_{\text{gs}}^*}{\partial z} = \frac{\partial}{\partial z} \left( D_{\text{eff}} \frac{\partial g_{\text{CO}}}{\partial z} \right) + 2 \eta_{\text{CO}} - \eta_{\text{CO}_2} + \eta_{\text{CO}_2}
\]

For the non-isothermal conditions it is modified into the differential form

\[
\frac{\partial \rho_{\text{app}}}{\partial t} + v_{\text{in}} \frac{\partial \rho_{\text{app}}}{\partial z} = \frac{n K_{\text{app}} (\rho_{\text{app}} - \rho_{\text{in}})^2}{K_{\text{app}} (\rho_{\text{app}} - \rho_{\text{in}})^2} \left[ \rho_{\text{app}} (\rho_{\text{app}} - \rho_{\text{in}})^2 \right]
\]

\( K_{\text{app}} \) is the rate constant which is deduced from the measurement of apparent density described in the Appendix. The apparent density \( \rho_{\text{app}} \) is converted to gaseous fraction \( g_{\text{gs}} \) using

\[
\frac{\partial g_{\text{gs}}}{\partial t} + \frac{\partial g_{\text{gs}} v_{\text{gs}}^*}{\partial z} = \frac{\partial}{\partial z} \left( D_{\text{eff}} \frac{\partial g_{\text{gs}}}{\partial z} \right) + \eta_{\text{gs}} - \eta_{\text{gs}}
\]

where \( v_{\text{gs}}^* \) is the molar average velocity of the gas phase.
The reaction is first order in $g_r$ and denoted as additional species. The rates of reactions (19) to (22) are expressed by the following expression:

$$
\frac{dH}{dt} = v_{wa}(z=H) \quad \text{(18)}
$$

### 3.5. Combustion Chemistry

The chemistry of carbon combustion within the powder packing is rather complex. There are two heterogeneous reactions, at low temperature formation of carbon dioxide according to

$$C + O_2 = CO_2, \quad r_1 \quad \text{........................................(19)}$$

and at high temperature the Boudouard reaction

$$C + CO_2 = 2CO, \quad r_2 \quad \text{........................................(20)}$$

Then, there is the homogeneous reaction $2CO + O_2 = 2CO_2$ between carbon monoxide, oxygen and carbon dioxide which occurs in steps. Many possibilities exist for the reaction steps depending on gas composition and temperature.$^{13}$

Here, we assume a simplified two-steps mechanism involving the reactions

$$CO + O_2 = CO_2 + O, \quad r_3 \quad \text{........................................(21)}$$

and

$$CO + O + M^+ = CO_2 + M^+, \quad r_4 \quad \text{........................................(22)}$$

So, atomic oxygen and a catalyzing species $M^+$ are introduced as additional species. The rates of reactions (19) to (22) are denoted as $r_1$, $r_2$, $r_3$, and $r_4$ and they are in mol per cm$^3$ powder packing and min.

The analytical expression for $r_1$ was deduced from an experimental investigation of carbon combustion in a casting powder packing in air.$^5$ There the reaction rate at $400^\circ$C was described with the equation $(1 - f)^{\alpha - 1} = kr$ where $f$ is the fraction of carbon combusted. This equation is equivalent to $df/dt = k(1-f)^{\alpha}$ with $f = g_c$ and $df/dt$ to $r_1$. Thus, $r_1 = k(1-f)^{\alpha}$. Assuming that the reaction is first order in $p_{CO}$ and including the reverse reaction yields $k = k_0 p_{CO} / x_{CO,eq} x_{CO,eq}$ with $x_{CO,eq} = x_{CO}/K_{(1)}$. Hence, the expression for $r_1$ becomes

$$r_1 = \frac{g_c^0 p_{CO}}{M_c} \left( \frac{g_c}{g_c^0} \right)^\alpha k_0 p_{CO} \left( x_{CO} - x_{CO,eq} / K_{(1)} \right) \quad \text{........................................(23)}$$

The exponent $\alpha$ was found to be 1.87 at $400^\circ$C. The temperature dependence of $k_0$ was derived from the experimental data at 300 and $400^\circ$C.

$$\log k_0 \, (\text{atm}^{-1} \text{ min}^{-1}) = -7590 \, T + 9.58 \quad \text{........................................(24)}$$

The rate equation for reaction (20) used by many authors is of the form $df/dt = k_0 p_{PCO} (1 + k_2 p_{PCO} + k_3 p_{PCO})$. But this does not give $df/dt = 0$ at equilibrium. So, a better equation is $df/dt = k_1 (p_{PCO} - p_{PCO,eq}) (1 + k_2 p_{PCO} + k_3 p_{PCO})$ with $p_{PCO,eq} = p^2_{PCO}/K_{(2)}$. According to this expression $f$ varies linearly with time, which can be set only initially. Later the rate decreases and at the end ($f \rightarrow 1$) it is zero. Thus, we set $k_1 = 0$, as Turkdogan and Vinters did, and applied the following expressions

$$\log k_1 \, (\text{atm}^{-1} \text{ min}^{-1}) = -13200 \, T + 9.68 \quad \text{........................................(26)}$$

$$\log k_2 \, (\text{atm}^{-1} \text{ s}^{-1}) = -5850 \, T - 3.97 \quad \text{........................................(27)}$$

$$k_3 = 0 \quad \text{........................................(28)}$$

The exponent $\beta$ is not known. We used $\beta = 1$. Alternatively, the same value of $\alpha = 1.87$ could be taken.

The rate equations for reactions (21) and (22) are deduced from the rate laws listed in combustion texts.$^1$ There, the rate is in mol per cm$^3$ gas phase and $s$, and the rate constant is given as $k = A \exp(-E/RT)$ with $A$ being in mol, cm, s depending on the order of the reaction. For the application in the present model these rates are to be multiplied with $60g_{c}^0$ to yield our $r's$ in mol per cm$^3$ powder packing and min. Thus the following equations are obtained for $r_1$ and $r_4$

$$r_1 = 60g_{c}^0 k_0^0 p_{CO} x_{CO} \left( x_{CO} - x_{CO,eq} / K_{(1)} \right) \quad \text{........................................(29)}$$

with

$$\log k_{CO,0} \, (\text{mol}^{-1} \text{ cm}^3 \text{ s}^{-1}) = -10450 \, T + 12.40 \quad \text{........................................(30)}$$

and

$$r_4 = 60g_{c}^0 k_0^0 p_{M} x_{M} \left( x_{CO} - x_{CO,eq} / K_{(4)} \right) \quad \text{........................................(31)}$$

with

$$\log k_{CO,M} \, (\text{mol}^{-2} \text{ atm}^{-1} \text{ cm}^6 \text{ s}^{-1}) = -990 \, T + 13.85 \quad \text{........................................(32)}$$

The content of the catalyzing species is taken to be

$$x_{M} = 0.4 x_{O} + 0.4 x_{N} + 0.75 x_{CO} + 1.5 x_{CO_2} \quad \text{........................................(33)}$$

The equilibrium constants of reactions (19) to (22) are obtained from the free energy data.$^{15}$
3.6. Boundary Conditions
The initial and boundary condition are applied as
\[
t = t_0 \quad \text{for} \quad 0 \leq z \leq H(t=0)
\]
\[
T = T_0, \quad \chi_{Ni} = 0.76, \quad \chi_{CO_2} = 0, \quad \chi_O = 0.21, \quad \chi_O = 0
\]
\[
t = t \quad \text{for} \quad z = 0
\]
\[
-\lambda_{eff} \frac{\partial T}{\partial z} = h(T - T_{furnace}), \quad \frac{\partial \chi_n}{\partial z} = 0, \quad \nu_1 = 0
\]
\[
t = t \quad \text{for} \quad z = H(t)
\]
\[
-\lambda_{eff} \frac{\partial T}{\partial z} = h(T - T_{wall})
\]
\[
x_{Ni} = 0.79, \quad \chi_{CO_2} = 0, \quad \chi_O = 0.21, \quad \chi_O = 0
\]
The heat transfer coefficient \(h_i\) between the furnace and the bottom of the quartz reaction tube is taken to be
\[
h_i = 2.9 \text{ W cm}^{-2} \text{ K}^{-1}
\]
which yields a reasonable time function of the heating rate. The heat transfer coefficient at the upper border of the powder column is chosen to follow the expression for natural convection \([16]\)
\[
h_2 = 2 \cdot 10^{-3} (T - T_{wall})^{0.25} \text{ W cm}^{-2} \text{ K}^{-1}
\]
3.7. Solution Technique
Due to the shrinkage of the packing during heating, its top surface moves downwards. Consequently, in an equidistant \(z\)-grid, the top moves through grid points. This causes difficulties in the finite difference computation at the top surface. To avoid the problem, the \(z\)-\(t\) system was transformed into an \(\eta\)-\(t\) system without movement of the upper surface, by setting
\[
\eta = \frac{z}{H(t)}
\]
where \(H(t)\) is the height of the solution domain (powder packing) at time \(t\). Thus, in the \(\eta\)-\(t\) coordinate system the top surface is always at \(\eta = 1\). An equidistant \(\eta\)-grid is used. This transformation requires the changes in several terms of the differential equations, i.e. the derivatives of a function \(q\) with respect to space coordinate \(z\) and time \(t\) are transformed as
\[
\frac{\partial q}{\partial z} = \left( \frac{\partial \eta}{\partial z} \right) \frac{\partial q}{\partial \eta} \quad \text{and} \quad \frac{\partial q}{\partial t} = \left( \frac{\partial \eta}{\partial t} \right) \frac{\partial q}{\partial \eta}
\]
The transformed equations are discretized and solved using the finite difference method. The computational flow chart is given in Fig. 6. The main difficulty was in the solution of the transport Eqs. (4) to (8) for the gaseous species, due to
the source terms containing the non-linear reaction rates \( r_i \). The explicit method would require very small time steps \( \Delta t \) (non-practical \( 10^{-6} \) min). So, the heat flow equation is solved explicitly and the transport equations of the gas implicitly using the Newton-Raphson and LU decomposition method. Iteration is needed until convergence is obtained for the average gas velocity, reaction rates and concentration distributions.

4. Modeling Results and Comparison with the Experiments

The model was run to calculate the heating-combustion behavior of the 5 cm high packing of casting powder in air. Figure 7 shows the development of the temperature profile in the powder packing from the start of heating to 120 min. The temperature at the bottom of the reaction tube increases from 27°C to become stable around 885°C in about 25 min. The profile does not reach complete steady state even after 2 h because the top of the powder packing keeps shrinking (and the combustion keeps going). The process of shrinkage is evident in Fig. 8.

The development of the carbon profile with time is given in Fig. 9, and Figs. 10 to 12 show the comparison between measured and computed profiles for the reaction times used in the experiments. There is very satisfactory agreement between the theoretical and experimental results, considering the inherent inaccuracies in the modeling of such complicated phenomena and in the experimental results. The figures demonstrate that the carbon minimum becomes more pronounced with increasing time, Figs. 10 and 11, and with increasing temperature at the bottom of the crucible, Figs. 10 and 12, as is to be expected. Figure 13 shows the off-gas analysis as a function of time, for the experiment with 120 min total time and 885°C final bottom temperature.
Both the carbon dioxide and carbon monoxide contents are low (smaller than 1 vol%), but the content of carbon dioxide is about three times larger than that of carbon monoxide over most of the reaction time. The maxima on the measured curves at about 50 min are possibly caused by an increase of diffusivity with decreasing carbon content due to a decrease of tortuosity. Such an effect is not taken into account in the model.

Figures 14 and 15 show the computed profiles of gas composition together with the carbon profiles, and the corresponding temperature profile together with reaction rate profiles for a time of 120 min. The reason for the shape of the various profiles is as follows. Oxygen from the air penetrates into the powder packing at the top surface but does not react yet according to reaction (19) since the temperature is low ($r_1$ in Fig. 15 is practically zero). That is oxygen and carbon monoxide coexist, and no carbon combustion takes place. Thus the carbon content stays unchanged. At some depth where the temperature is high enough reaction (19) starts and carbon is combusted with oxygen to carbon dioxide. Thus, the first minimum of carbon content develops (zone 2). Still deeper all the oxygen is consumed and both the carbon dioxide and $r_1$ obtain a maximum, but carbon dioxide does not oxidize carbon yet because the temperature is too low ($r_2$ is practically zero). Hence, no combustion takes place and the carbon content stays high (zone 3). Part of the carbon dioxide diffuses downwards to the bottom part of the column where the temperature is high enough for the Boudouard reaction (20). So, carbon starts...
to combust there by carbon dioxide and the second carbon minimum develops (zone 4). Rate $r_2$ has its maximum at the bottom where the temperature is highest. The carbon monoxide formed by the Boudouard reaction diffuses upwards and combusts with oxygen in the upper part of the column according to reaction (21) and (22). Some of it leaves the powder at the top.

5. Summary and Conclusions

The combustion of carbon in a packing of casting powder has been investigated under thermal conditions similar as in continuous casting. In the experimental part of the study powder samples of about 5 cm height were heated one-dimensionally in a heating apparatus with the top of the sample being at low temperature and exposed to air. After the reaction the carbon content was determined along the powder column. A characteristic profile had developed with two carbon minima, one in the region of moderate temperature ($\approx 500^\circ$C), caused by combustion with oxygen, and the other in the region of elevated temperature ($\approx 750^\circ$C), due to combustion with carbon dioxide. It is interesting that the high temperature minimum did not reach zero carbon content. This may also happen in the real continuous casting mold. That is residual carbon may still be present on sintering which then enters into the slag pool causing carbon pick up of the steel. The mathematical model was developed for the interpretation of the experimental results. It involves the solution of the rate equations for four combustion reactions and of the differential equations for heat and mass transport. The theoretical results confirm the measured carbon profiles and off-gas compositions.

The model describes adequately the phenomena in the upper part of the powder packing in the mold where the powder is still loose, or slightly sintered but still has interconnected pores. It may be applied also to the deeper zones where melting commences provided that sintering and melting occurs uniformly without formation of holes and large slag globules. This is the case for premelted powders. Also a two- or three-dimensional fluid flow model for the pool region may be added for the treatment of the slag transport to the gap at the mold faces so that a complete model becomes available for monitoring the behavior of the casting powder on heating and melting, and its consumption during the continuous casting process.

Acknowledgement

The authors wish to thank Stollberg GmbH for providing the premelted powder.

Nomenclature

- $c_{i}$, $c_{g}$: Concentration of individual gas species and of gas (mol cm$^{-3}$)
- $c_{C}$: Molar density of graphite ($=\rho_{C}/M_{C}$)
- $D_i$, $D_{eff}$: Diffusivity and effective diffusivity of gas (cm$^2$ min$^{-1}$)
- $f_{C}$: Mass fraction of carbon
- $g_C$, $g_{g}$, $g_{ox}$: Volume fraction of carbon, gas and oxide
- $g_{C*}$: Initial volume fraction of carbon
- $h_{1}$, $h_{2}$: Heat transfer coefficient at the bottom and at the top of powder column (W cm$^{-2}$ K$^{-1}$)
- $H$: Height of casting powder column (cm)
- $H_C$, $H_{g}$, $H_{ox}$: Enthalpy of carbon, gas or oxide (J g$^{-1}$)
- $\bar{H}$: Enthalpy of individual gas species (J mol$^{-1}$)
- $k_{p}$, $k_{i}$: Rate constant
- $K_{C1}$, $K_{C2}$, $K_{C3}$, $K_{C4}$: Equilibrium constant of reactions (19), (20), (21) and (22)
- $k_{i}$: Rate constant for sintering equation
- $M_{C}$: Molecular mass of carbon (12.011 g mol$^{-1}$)
- $p$: Total pressure of gas (1 atm)
- $q$: Arbitrary function to be transformed
- $r_{1}$, $r_{2}$, $r_{3}$, $r_{4}$: Rate of reactions (19), (20), (21) and (22) (mol cm$^{-3}$ powder packing min$^{-1}$)
- $t$: Time (min)
- $T$, $T_0$: Temperature, initial temperature of casting powder (K)
- $T_{air}$, $T_{furnace}$: Temperature of air, above column and of furnace below powder column (K)
- $v_{C}$, $v_{i}$, $v_{ox}$: Velocity in $z$ direction of carbon, individual gas species and oxide (cm min$^{-1}$)
- $v_{g*}$: Molar average velocity in $z$ direction of gas (cm min$^{-1}$)
- $v_{z}$: Velocity in $z$ direction (cm min$^{-1}$)
- $x_{i}$: Mole fraction of individual gas species
- $z$: Height coordinate (cm)
- $\eta$: Transformed dimensionless height coordinate ($=z/H$)
- $\lambda_{eff}$, $\lambda_{gas}$, $\lambda_{solid}$: Effective thermal conductivity, thermal conductivity of gas and of solid oxide (W cm$^{-1}$ K$^{-1}$)
- $\rho_{app}$, $\rho_{C}$, $\rho_{g}$, $\rho_{ox}$: Apparent density of casting powder, density of carbon, gas and oxide (g cm$^{-3}$)
- $\rho_{app}^{s}$, $\rho_{s}$: Initial apparent density of casting powder, density of solid in the powder (g cm$^{-3}$)
- $\tau$: Tortuosity factor

Subscript

- $eq$: Equilibrium value
Appendix. Measurement of Apparent Density

The apparent density is an important modeling parameter which has to be well known in order to obtain realistic simulation results. It is directly related to the pore fraction of the packing which in turn determines the effective diffusivity of the gaseous species in the packing and the effective thermal conductivity of the casting powder. Therefore, in the present study the apparent density of the used powder was measured as a function of temperature. The powder was carefully packed in a pre-weighed alumina crucible in such a way that the initial density was approximately the same for each sample of a particular powder. Then the crucibles were placed in a muffle furnace and heated for 2 h at temperatures between 200 and 1 000°C. Afterwards, the samples were taken out of the furnace and cooled to room temperature in a desiccator to prevent pick up of moisture. For the powders containing carbon, the heating was carried out under an argon atmosphere in order to avoid the oxidation of the carbon.

The mass was obtained by weighing with a sensitive electronic balance. The volume measurements were carried out with two methods depending on heating temperature. The samples heated to below 600°C had a small degree of sintering. They were still brittle and could not be taken out of the crucible. The shrinkage of the packing was little and only in height. Therefore, in these experiments the volume was determined from the height of the powder packing and the known cross sectional area of the crucible. The samples heated above 600°C sintered into a solid non-symmetric body that could be taken out of the crucible. Their volume was determined by measuring the volume of water displaced by the body during immersion in water, applying Archimedes’ principle. To avoid penetration of water into the sample, the surface connected pores were sealed with wax. The measured density values are averaged from several measurements and plotted against temperature in Fig. A1.

The apparent density data are used to estimate the constant $K_s$ in the rate equation for sintering (Eq. (15)) taking $\tau=120$ min. The numerical values obtained for the powder with 5 mass% graphite are: $K_s(400°C)=0$, $K_s(600°C)=0.036$, $K_s(800°C)=0.045$, $K_s(1 000°C)=0.361$ min$^{-1/2}$ when $n$ is taken to be 0.5.