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THERMOKINETICS OF THE COMBUSTION OF CARBON CONTAINING MATERIALS

Practical aspects of the investigations

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Abstract

The results of the thermokinetic analysis of the combustion of carbon containing materials in the air and oxygen have been presented. A thermokinetic model has been developed, which simplifies the current approach assuming the 0-th order and zero activation energy for this process. The interpretation of the results makes possible the identification of the material (carbon carrier) of the highest reactivity toward oxygen. This material was used as a component of the insulating grease fill for the continuous slab caster (CSC) process. The application of the fill proves successul in the industrial practice.

Keywords: air, coal, combustion, continuous slab caster process, graphite, grease, oxygen, reactivity

Introduction

The investigations of the thermokinetics of the combustion of the coal/graphite materials can be used for a formation of the criterion estimating their usability in processes taking place under strong oxidative conditions. The continuous slab caster (CSC) process is one of such processes in which the carbon containing materials can be used as a component of the insulating greases in a mould (Fig. 1, position 4). The carbon containing material supplies heat which is necessary for the transformation of the grease fill into a liquid form. Additionally, the gases evolved during this process fluff the slag film formed. Most often the highly disintegrated natural or waste graphite, quick cokes, carbonaceous materials and some blacks are used as carbon carrier [1].

Generally the nature and the rate of oxidation of carbon carriers significantly depends upon:

the type of the oxidative medium: O_2 (air), CO_2, water vapour,
thermal and pressure conditions,
physical and chemical characteristics of the coal/graphite material.

The structure, crystallographic form, porosity and inorganic matters of the catalytic or inhibitory character can be mentioned as the most important factors influencing the oxidation process [2].

The aim of this work is to design a criterion of the usability of the commercial and waste carbon carriers as the components for insulating greases for the CSC process.

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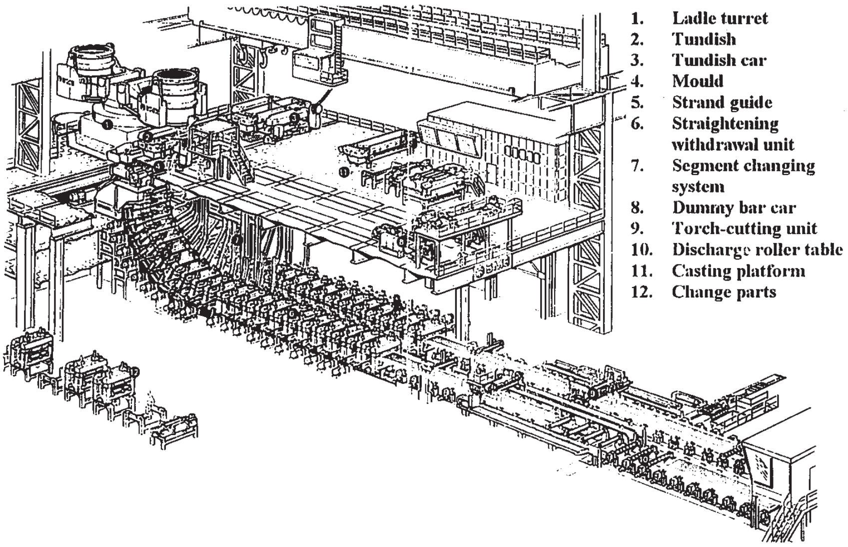

Fig. 1 The SMS installation for continuous slab caster (CSC) process, according to [3]

Industrial tests

The tests of a few greases of similar composition, but containing different carbon carriers have been performed as a continuation of our previous investigations [1].

The greases have been tested on one line of the CSC, while using the Melubir produced by the French DAM and Scorialit of the German Metallurgica. It was found that some carbon carriers can be used as components of insulating greases. In these cases the visual inspection of the ingot obtained under the grease tested revealed the surface of the comparable quality as that resulted from the treatment performed with the greases of the best producers.

However, some unexpected effects have also been observed. Under the grease containing one of the graphite component the freezing process of the slag formed from this grease occurred in mould, which can result in a steel effluent, and a failure of the CSC installation. This effect can be explained by too rapid combustion of the carbon contained in the grease which resulted in the lack of heat source. We performed systematic investigations aimed at setting an optimal phase composition of the grease.

Thermogravimetric studies

Five commercial and waste carbon containing materials of different origin were selected for these investigations. The tests were performed using the samples of the grain sizes under 0.063 mm. Physical and chemical characteristics are given in Table 1. The Perkin Elmer 2400 apparatus was used for the determination of carbon and hydrogen content.

Table 1 Characteristics of the carbon containing materials that are used for the study

Symbol	Origin of the material	Moisture/	A^d/	V^{daf}/	C^d/	H^d/
		mass %				
C1	natural graphite	0.3	7.1	2.1	92.64	0.09
C2	bulk scrap graphite	0.4	4.0	0.6	91.25	0.08
C3	commercial graphite dust prepared from the scrap material	0.2	1.4	0.9	93.50	0.00
C4	waste graphite – dust	1.0	19.1	2.2	80.70	0.12
C5	breeze coke	0.5	9.2	1.3	84.76	0.25

Thermogravimetric analysis was performed in the MOM Q-1500D apparatus under the following protocol: reference substance: α-Al_2O_3, initial mass of the sample m_i=100 mg, heating rate q=10 K min^{-1}, final temperature 1273 K, atmosphere: air-static, oxygen-dynamic, a plate-like melting pot of platinum (1 plate).

Results

There are only a few works among these concerning the combustion of carbon containing materials using thermogravimetric techniques which deal with problems being analyzed in our work [4–11]. It should be mentioned here that there is no need to assume a classical thermokinetic equation at the first order, as given in [7–8], because the results presented (Figs 3 and 6 in [8]) clearly indicate the linear dependence between mass loss on heating and temperature.

The exothermic process of combustion taking place in such conditions, above a certain temperature can be treated as a 0th order kinetics of very low activation energy which can be neglected.

Therefore, we are obtaining a linear relationship describing the mass on heating as a function of temperature T:

$$m=\frac{k}{q}(T_f-T),\ \text{when } m_i=\text{constant} \quad (1)$$

The kinetic constant k takes a dimension of mg min^{-1} and T_f is an estimated theoretical final temperature of combustion. Practically, the T_f temperature equals to the real final temperature of combustion only for the samples that do not contain any mineral substance, i.e. 100% of the sample evolves the reaction as gases. In order to study the variability of the T_f parameter it is recommended to set an initial weighted portion of the sample m_i at a constant value.

For the TG curves obtained during the combustion of carbon containing materials in the air (Fig. 2) the range of the best fit of experimental data to the model(1) assumed is determined.

The analysis of the results allows us to observe that kinetic constant describing the combustion takes similar values for all carbon carriers (Table 2). Therefore, it is difficult to estimate the oxidability of the coal/graphite substance basing on the con-

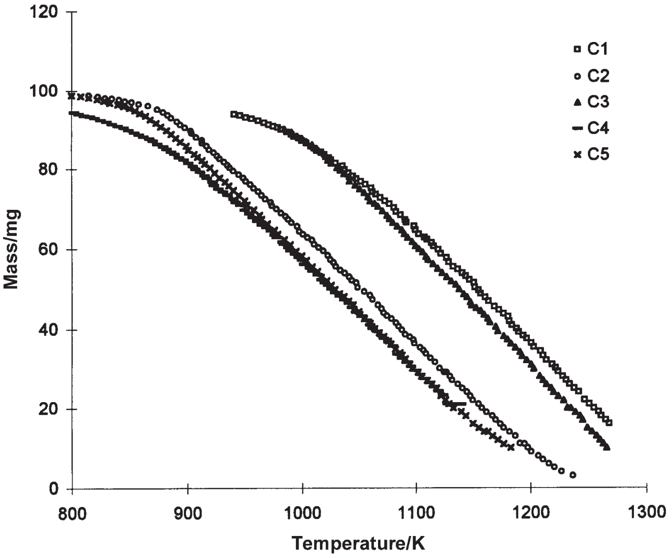

Fig. 2 The TG curves characterizing the combustion of carbon containing materials in the air

stant value. It is a values of the final temperature of combustion that are much more differential. For the C1 carrier this parameter evidently takes a higher value.

Table 2 Kinetic parameters of the combustion of some carbon containing materials in the air

Carbon carrier	Rate of combustion k/ mg min^{-1}	T_f/K	Linear determination coefficient r^2
C1	2.515	1347	0.9879
C2	2.574	1242	0.9932
C3	2.508	1305	0.9693
C4	2.204	1255	0.9828
C5	2.580	1220	0.9856

The fact that a rate of combustion in the air can be limited both by the low concentration of the oxidative medium, and a low diffusion rate of this medium inspired us to perform thermogravimetric investigation in oxygen. The sample mass was reduced to 70 mg, and we used 4 plates in order to minimize the influence of the heat supplied during combustion of the sample on the increase of temperature in the oven. Also for such conditions, the TG curves are linear almost within all ranges. The results of thermokinetic analysis of the curves obtained are shown in Table 3.

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Table 3 Kinetic parameters of the combustion of some carbon containing materials in oxygen

Carbon carrier	Rate of combustion k/ mg min^{-1}	T_f/K	Linear determinance coefficient r^2
C1	3.669	1199	0.9871
C2	2.961	1151	0.9978
C3	6.991	1111	0.9837
C4	3.565	1101	0.9211
C5	5.294	1000	0.9747

The comparison of the values of T_f and k obtained for oxygen with those determined in the air allows us to the observation of significant increase in the reaction rate k accompanied by the decrease of final temperatures T_f. The differentiation of the kinetic constant is much higher for oxygen atmosphere than for the air.

Conclusions

The method developed for the analysis of the combustion of carbon carriers on the basis of thermokinetic analysis allows one for the initial estimation of the usability of the coal/graphite materials for the production of the insulating greases for the CSC process.

It is the C1 carrier indicating the lowest oxidability that appeared the most useful as a component for the production of the high quality insulating greases for the CSC processes. The investigations of the combustion rate of the substances containing carbon should be performed in oxygen, which makes this rate depending upon the characteristics of the material, and not upon the concentration and diffusion of the oxidizing agent to the reaction site as observed while combustion in the air.

List of symbols

A^d	ash in a dry sample, mass%,
k	rate constant of combustion, mg min^{-1},
m	mass at T, mg,
m_i	initial mass of the sample, mg,
q	rate of heating, K min^{-1}
r^2	linear determinance coefficient, $0 \leq r^2 \leq 1$,
T	temperature, K,
T_f	finical, theoretical temperature of a combustion, K,
V^{daf}	volatile matter in a dry and ash free sample, mass%.

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