Journal of Thermal Analysis and Calorimetry, Vol. 77 (2004) 201–206

OXYREACTIVE THERMAL ANALYSIS
A good tool for the investigation of carbon materials

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Abstract

The paper presents the applicability of Oxyreactive Thermal Analysis (OTA) for the investigation of different kinds of carbon matter. For comparative reasons and more precise interpretation, along with OTA some physico-chemical properties of analyzed materials were used as the methods commonly applied for the investigations.

The carbon materials of both natural (anthracites, graphite and diamonds) and synthetic origin (active carbon, glass carbon, expanded graphite, soot and synthetic diamonds) were investigated.

It was stated that there is close relationship between structure parameters and physico-chemical properties and the thermal reactivity within the investigated groups of carbon matters. The results show that OTA can be accepted as a good investigative way for such materials.

Keywords: anthracites, diamonds, graphites, reflectance/bireflectance, synthetic carbon materials, thermal analysis

Introduction

The question of ambient oxyreactive conditions during the thermal analysis of organic substance and carbon matter has been discussed in the literature since 1994. The literature concentrates mainly on geoscience problems and on investigations of the natural environment. In the last time some investigations are concentrated also on other problems such as: studies of catalytic oxidation of carbon matter [1], SO binding into semicoke and coals during thermooxidation [2], thermal decompositions of Fullerene [3].

In the work presented here, the authors would like to draw attention to the wide range of these investigations and to the application of thermal analysis methods in the investigation of all types of carbon materials.

The methodological aspects of Oxyreactive Thermal Analysis (OTA) are extensively reviewed in the work of Cebulak and Langier-Kużniarowa [4]. The basic rule of the OTA method is the optimization of the experimental conditions so that the stoichiometric requirements for the oxidation reactions are completely met.

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The results presented here for OTA analyses of various types of carbon matter (of both synthetic and natural origin), carried out under such optimal conditions, show that the results can be the basis for a general broadening of the range of materials that may be investigated. The results can also be used to evaluate the structural differentiation and technological properties of carbon matter.

Methodology

The analyses were carried out using the 34-27T derivatograph made by the MOM (Hungary) company and using the Paulik–Paulik–Erdey system. The conditions of the analyses were as follows: a dynamic air atmosphere, a set of small platinum plates as sample holder, a sample dilution in Al_2O_3 of 1:3 (20:60 mg), an optimal grain size and a heating rate of 10°C min^{-1}. To evaluate the results of the investigation, the data from the OTA analyses are compared with the results of measurements of bireflectance values.

Results

The OTA data for the range of carbon materials examined are shown on a set of DTA curves for diamond, graphite (Fig. 1) and anthracite and many synthetic forms of car-

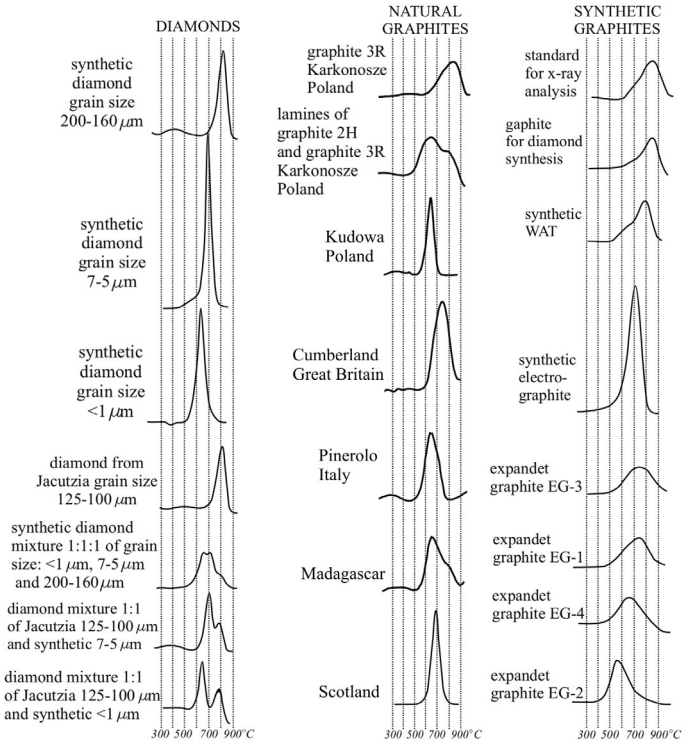

Fig. 1 DTA curves of diamonds and graphites

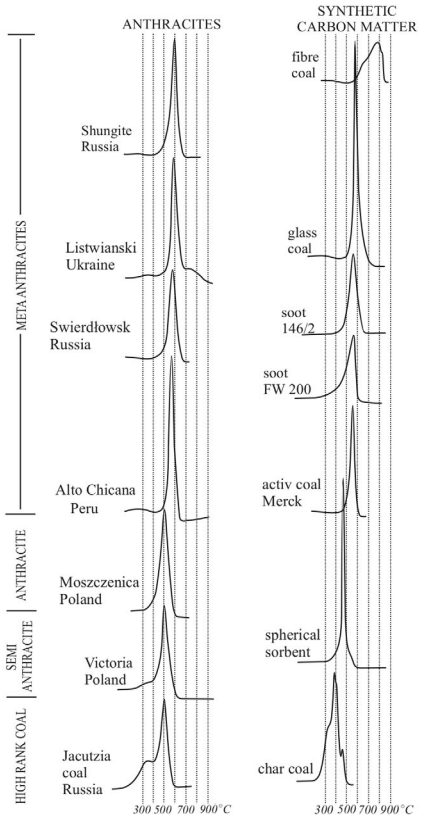

Fig. 2 DTA curves of anthracites and different synthetic carbon materials

bon matter (Fig. 2). Each carbon material can be defined by the progress of the reaction and a characteristic maximum temperature of oxidation.

Diamonds

The results show one, regular and rapid oxidation reaction and its occurrence at high temperature (640–820°C). The temperature is clearly dependent on the size of the diamond grains. The results show the usefulness of OTA in the evaluation of the diamond-grain size fractions.

Graphites

This group of carbon matter is characterized also by high-temperature (560–840°C) oxidation reactions. The temperatures are higher for natural graphites and more variable, from low to very high, for synthetic graphites (Fig. 1). The OTA data enable to differentiate between structural types of graphite (2H and 3R). The temperatures

and the progress of the reactions are typically very different. This indicates probably that the graphite structures are not monotypic and that the sizes of individual crystallites are different.

Graphite is an important geochemical indicator. The results of earlier investigations [5–8] document a clear dependence between graphite oxyreactivity and variation in physicochemical conditions during its formation. The influence of compositional variability of the primary graphite is also important. These interdependences were the basis for the industrial use of graphite materials. Graphite materials are used in many ways because of the variety of their technical properties. The DTA curves of some synthetic graphites (Fig. 1) show the importance of OTA analyses in their investigation. The correlation between OTA data from expanded graphites and their sorptive properties (Table 1) is a good example of this importance.

The OTA results of four different exfoliated graphites (EG) (used as sorbents for oils) show convergence with technical parameters (Table 1). The graphite (EG-3) showing the highest-temperature oxidation reaction is that with the highest sorptivity. However the detailed investigations show that the sorption capacity of the EG-3 graphite decreases drastically while using the sorbent in practice. The EG-4 graphite is more effective sorbent.

Table 1 The sorptive properties of the expanded (exfoliated) graphites (Morawski A. W. and Tryba B., 2002 unpublished)

Sample	BET surface area /m^2 g^{-1}	Bulk density /kg m^{-3}	Sorption capacity	
			5w/40	15w/40
Expanded Graphite EG-3	77.4	1.5	55.3	61.0
Expanded Graphite EG-1	68.7	7.0	40.0	33.5
Expanded Graphite EG-4	57.7	4.0	46.0	54.8
Expanded Graphite EG-2	111.7	10.0	33.7	43.8

Anthracites

In the case of anthracites the temperatures of oxidation reactions are lower (500–600°C) and the reactions are characterized by obviously high rates (Fig. 2). Differences in the character of their oxidation reactions are well correlated with the respective differences in their composition and structure. The details of the DTA curves reflect the variations well. Differences correlate with physico-chemical properties as revealed by bireflectivity investigations ([9]; see also Fig. 3). There are visible differences between metaanthracites (shungite and Listwianski), anthracite, semianthracite (the Moszczenica anthracite) and coal from Jacutzia. The character of the oxidation reactions, as seen in OTA results, correlate well with physico-chemical parameters that reflect progress in structural transformation of carbon matter in the range from high-rank coal to meta-an-

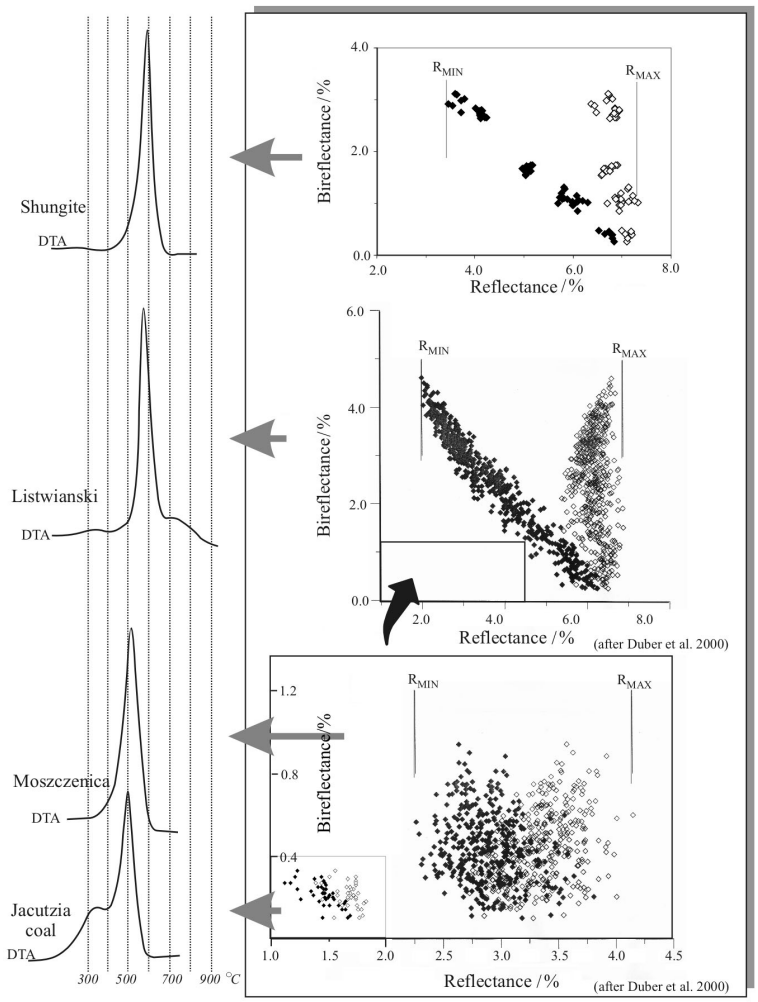

Fig. 3 The comparison of the oxyreactivity and Kilby cross-plots (measured R'_{min} and R'_{max} values *vs*. bireflectivity) of some anthracites

thracite. Such comparison of the results from OTA analysis with the results of other techniques and investigative methods is of very interest.

Synthetic carbon matter (SCM)

The carbon materials are characterized by great variation in the progress of the oxidation reaction. The convergence of resolved forms of SCM with those of natural carbon matter (NCM) is clear as is that of fibrous coal with graphite, glassy coal with metaanthracite and active coal with anthracite comparable to semi-anthracite.

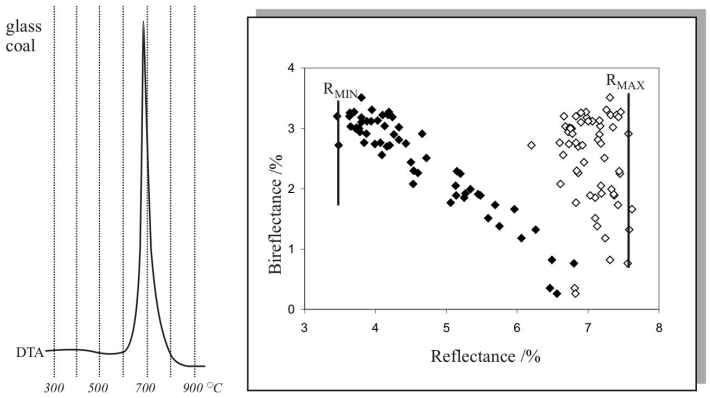

Fig. 4 The comparison of DTA curve and reflectance values (Kilby cross-plot) obtained for glass coal

On the basis of OTA results, the glassy coal is very similar to meta-anthracite (Fig. 2). Bireflectivity results (Fig. 4) support that comparison. The coal is characterized by a lower degree of structural order and higher average value of the R_{max} parameter.

The range of OTA results correlates well with the properties revealed by optical microscope investigations and other technics. The OTA results, particularly the variable dynamics of the oxidation reaction, are well explained also in terms of the variability of their technical properties. The comparison of the dispersal of the OTA results for active coals and spherical carbon sorbent with the variability of the sorptive properties is very characteristic.

Conclusions

- The results of these investigations confirm the original premise.
- OTA investigations of carbon material can be the basis for the evaluation and recognition of physico-chemical properties, even of extremely variable types of carbon.
- The TA analysis should be carried out under precise conditions required for oxidation of the carbon material involved.

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