Thermochimica Acta, 51 (1981) 25—31
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

VACUUM BALANCE AND RELATED STUDIES OF CARBONS USED IN ZINC-LEAD PRODUCTION

MARGARET A. CARTER, D.R. GLASSON and S.A.A. JAYAWEERA
John Graymore Chemistry Laboratories, Department of Environmental Sciences,
Plymouth Polytechnic, Plymouth, PL4 8AA, Devon, England

ABSTRACT

The reduction of metal oxide to metal is an essential step in the extractive metallurgy of zinc and lead. The performance of metallurgical cokes in this reaction is governed by inter alia, their reactivity. In this research the reactivity of selected carbons, including some metallurgical cokes, is investigated as follows. The surface and solid state properties of the materials are examined by vacuum microbalance and microscopic techniques. Their oxidation is studied by thermogravimetry and differential thermal analysis. The extent of reaction is correlated with reaction conditions, for example, temperature and time of oxidation, flow rate and surrounding atmosphere, and particle size, porosity and crystallinity of the carbons.

The nitrogen adsorption isotherms of the carbons were recorded at -196°C on a CI Mark II microbalance; specific surface areas were calculated by the BET method. The oxidations were carried out on a Stanton-Redcroft mass flow balance, model MF-H5; the TG and DTA curves were recorded simultaneously on the same sample. The crystallinity and particle size were characterised by scanning and transmission electron microscopy (Jeol SEM35 and Philips EM300 electron microscopes).

Results are presented for a selection of charcoals, graphites and cokes.

INTRODUCTION

Production of zinc and lead by pyrometallurgical processes require metallurgical cokes of suitable reactivity (1). They are usually hard low-reactivity cokes from high-temperature carbonisation (900-1050°C). In zinc-lead blast furnace practice, the reducing agent is carbon monoxide produced from the coke with air blast. Since zinc oxide has a high heat of formation, reduction only commences at temperatures as high as 1100-1300°C, dependent also on the nature of the lump oxide or lump sinter from prior roasting of the sulphide ores. Thus a good metallurgical coke for this process must have an

0040-6031/81/0000—0000/$02.75

optimum combination of physical and chemical properties, notably particle shape, strength, high carbon content and low reactivity. Since prime coking coal is becoming less readily available, "formed" cokes have been developed in which blends of "non-coking" coals are incorporated into the briquettes.

In the present research, the microstructure of types of both (soft) graphitising and (hard) non-graphitising carbon were studied, including graphite used in the steel industry and coke and coal char used in zinc production. The surface and solid-state properties of the materials were examined by vacuum microbalance and microscopic techniques. Their oxidation, studied by TG and DTA, was correlated with reaction conditions, e.g. temperature and time of oxidation, flow rate of the surrounding atmosphere and particle size, porosity and crystallinity of the carbons.

EXPERIMENTAL

Surface areas of the materials were determined by a gravimetric B.E.T. method (2), using nitrogen gas sorption at -196°C recorded on a vacuum microbalance, CI Microforce Mark 2B, which gave µg to mg sensitivity, using samples of 0.25 g or less. The adsorption isotherms also indicated any micro- or meso-porosity present (from hysteresis) and pore size ranges. Average crystallite sizes (equivalent spherical diameters) deduced from the specific surfaces of the less porous materials were compared with aggregate sizes observed by optical- and electron-microscopy (Jeol SEM 35 and Philips EM 300). Macroporosity of some of the materials was determined by liquid displacement.

Preliminary TG and DTA studies of the oxidation of some of the samples were made, using a Stanton-Redcroft Mass-flow Balance, MF-H5.

RESULTS AND DISCUSSION

Micro-structure of Nantgarw coke, Australian coal char and PMC graphite

Cokes have pregraphitic structure, since during their formation they pass through a plastic phase (when the smaller structural units can align), whereas chars do not pass through a plastic phase, so that they can be expected to have a structure related to the parent material.

The Nantgarw coke and the PMC graphite gave type II nitrogen adsorption isotherms (Fig. 1).

The B.E.T. equation was applicable to the lower relative pressure ranges (0.05 to 0.30) of the isotherms to determine the surface areas of the materials, from which the average crystallite sizes could be deduced using the X-ray density value of 2.266.

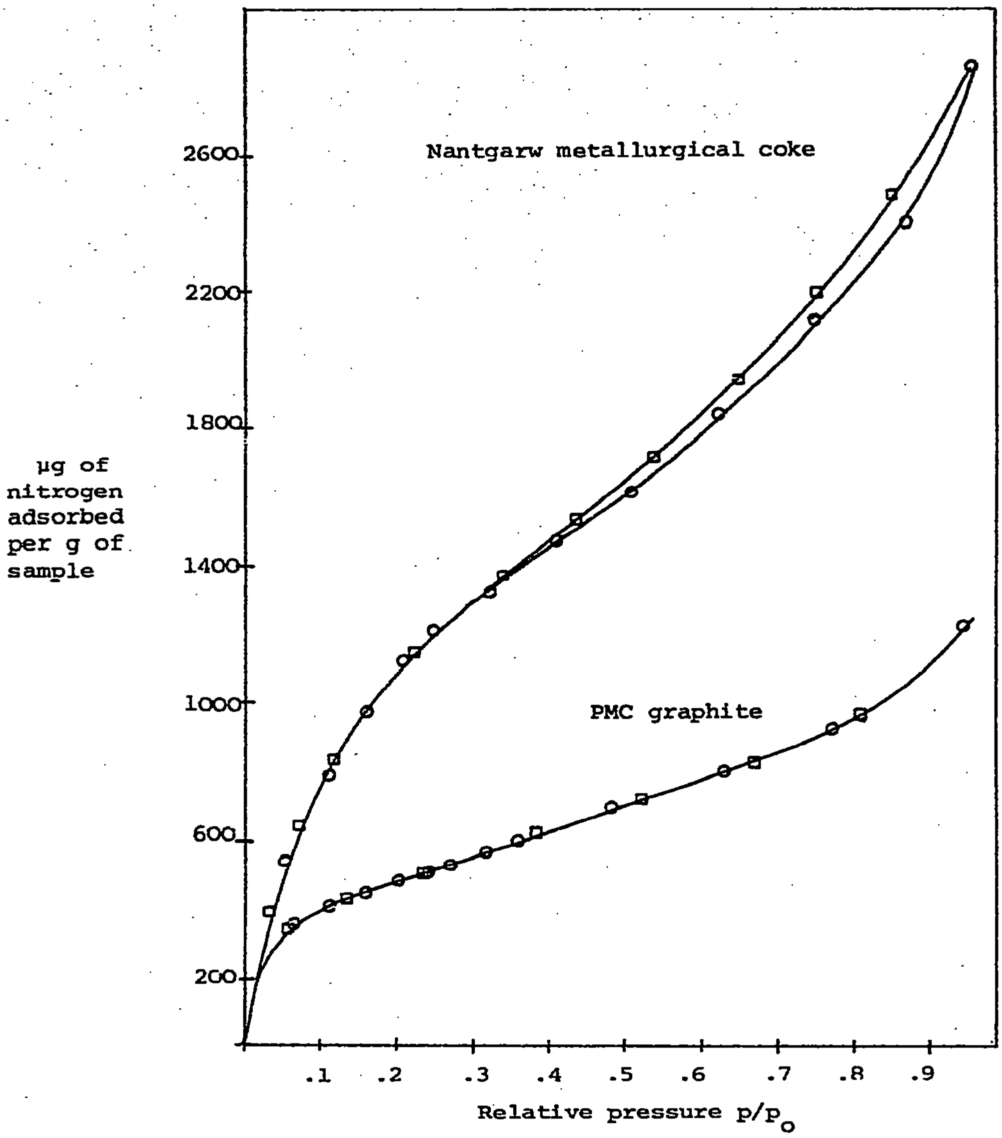

Fig. 1. Adsorption of nitrogen at -196°C on Nantgarw coke and PMC graphite.

The PMC graphite had the lower surface area of 1.4 m^2g^{-1} compared with 3.6 m^2g^{-1} for the Nantgarw coke, corresponding to average crystallite sizes of 1.9 and 0.74 μm respectively.

The PMC graphite has no micro- or meso-porosity, since no adsorption hysteresis was shown. The Nantgarw coke had no microporosity and only a limited amount of meso-porosity (pore sizes of 20-500 A widths), showing adsorption hysteresis only above a relative pressure of 0.35. Both samples had macroporosity (pore sizes over 500 A), as evidenced from apparent density measurements by liquid displacement (compared with the X-ray density of graphite)

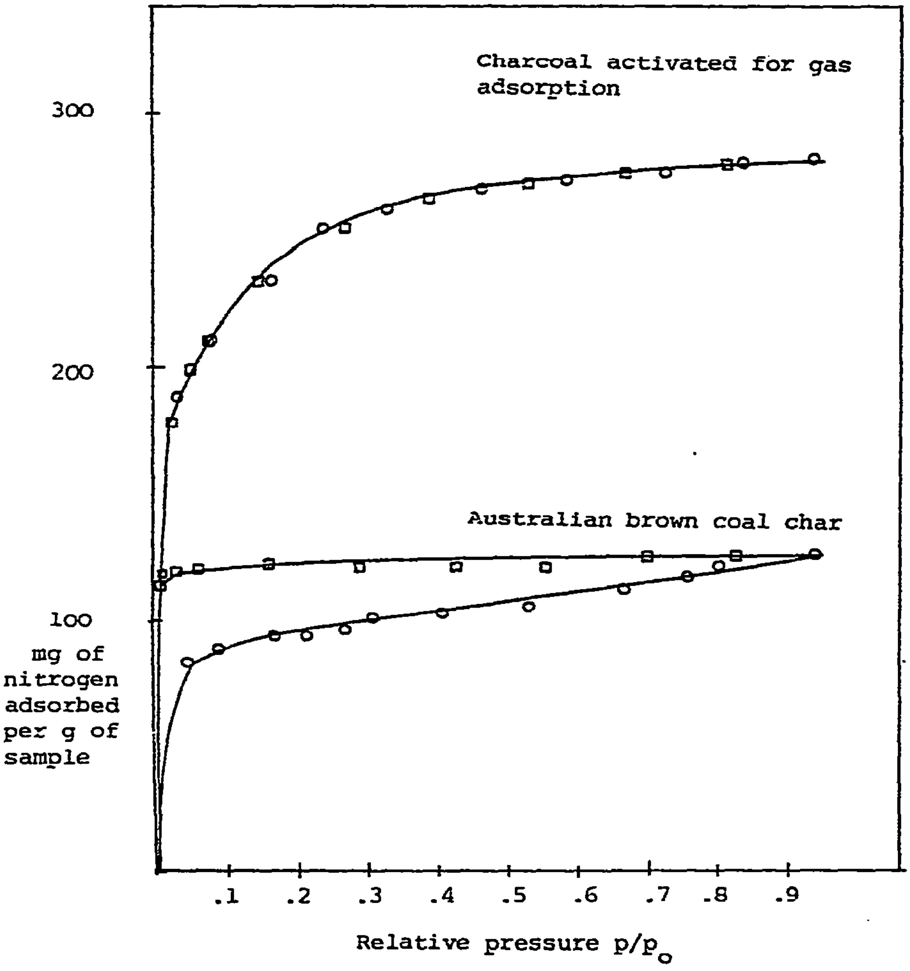

Fig. 2. Adsorption of nitrogen at -196°C on Australian brown coal char and charcoal activated for gas adsorption.

which indicated pore volumes of 13% for PMC graphite and 40% for Nantgarw coke (less a small amount of mesopore volume for the latter). Low magnification scanning electron-micrographs showed the irregular shape and pitted surface of the Nantgarw coke. Its graphitic nature could be seen in the transmission electron-micrographs, with sharp edges to the particles.

The Australian brown coal char gave a type I isotherm like a sample of activated charcoal (Fig. 2). The hysteresis loop for the coal char closed only at very low relative pressures, indicating considerable porosity with a full range of micro- and meso-pore sizes. Surface areas were calculated from a Langmuir plot and are shown in Table I.

Optical microscopic observations showed that the Australian brown coal char lumps vary from 0.5 to 5 mm. Low power scanning electron-micrographs showed

TABLE 1

Specific surfaces of carbons

Material	Isotherm type	Specific surface, m^2g^{-1}
Nantgarw coke	II	3.6
PMC graphite	II	1.4
Australian brown coal char	I	410
Charcoal activated for gas sorption	I	948
Chromatographic charcoal	II	824
Decolourising "Norit GSX" Charcoal	II	824
Decolourising HW 299200 Charcoal	II	698

that the surface has no large indentations like the Nantgarw coke and transmission electron-micrographs showed no sharp edges to the particles.

Chromatographic and decolourising charcoals

Samples of chromatographic and decolourising charcoals gave type II nitrogen adsorption isotherms, showing no microporosity but some mesoporosity, (Fig. 3), with pore sizes covering most of the range (20-500 A). A sample of Norit gave an adsorption isotherm almost identical with that of the chromatographic charcoal. Specific surfaces calculated from the isotherms by B.E.T. plot are shown in Table 1.

Oxidation of Nantgarw metallurgical coke

In Fig. 4, TG and DTA data are presented for the oxidation of Nantgarw coke in static (fully-lined curves) and in flowing air (broken-lined curves), for a heating programme of $5^{\circ}C\ min^{-1}$ rise in temperature. In static air, oxidation takes place mainly between 600-900°C, with a broad exotherm over this temperature range. The oxidation occurs at correspondingly lower temperatures in flowing air (mainly between 500-850°C) and the DTA exotherm separates into 2 peaks at about 650° and 800°C. This behaviour contrasts with that of the finer materials (chromatographic and decolourising charcoals) which give only a single sharper DTA peak which is shifted slightly by flowing air to lower temperatures. The 2 peaks given by the granular materials (Nantgarw coke, PMC graphite, Australian brown coal char and charcoal activated for gas sorption) are ascribed to changes in the oxidation kinetics, in that at higher temperature the rate is diffusion-controlled (3,4).

Preliminary experiments have been done on reduction of coke and char reactivity by additives such as boric oxide, B_2O_3. Thus the pore volume of the Australian brown coal char is reduced when it is heated with B_2O_3 (at about 450°C).

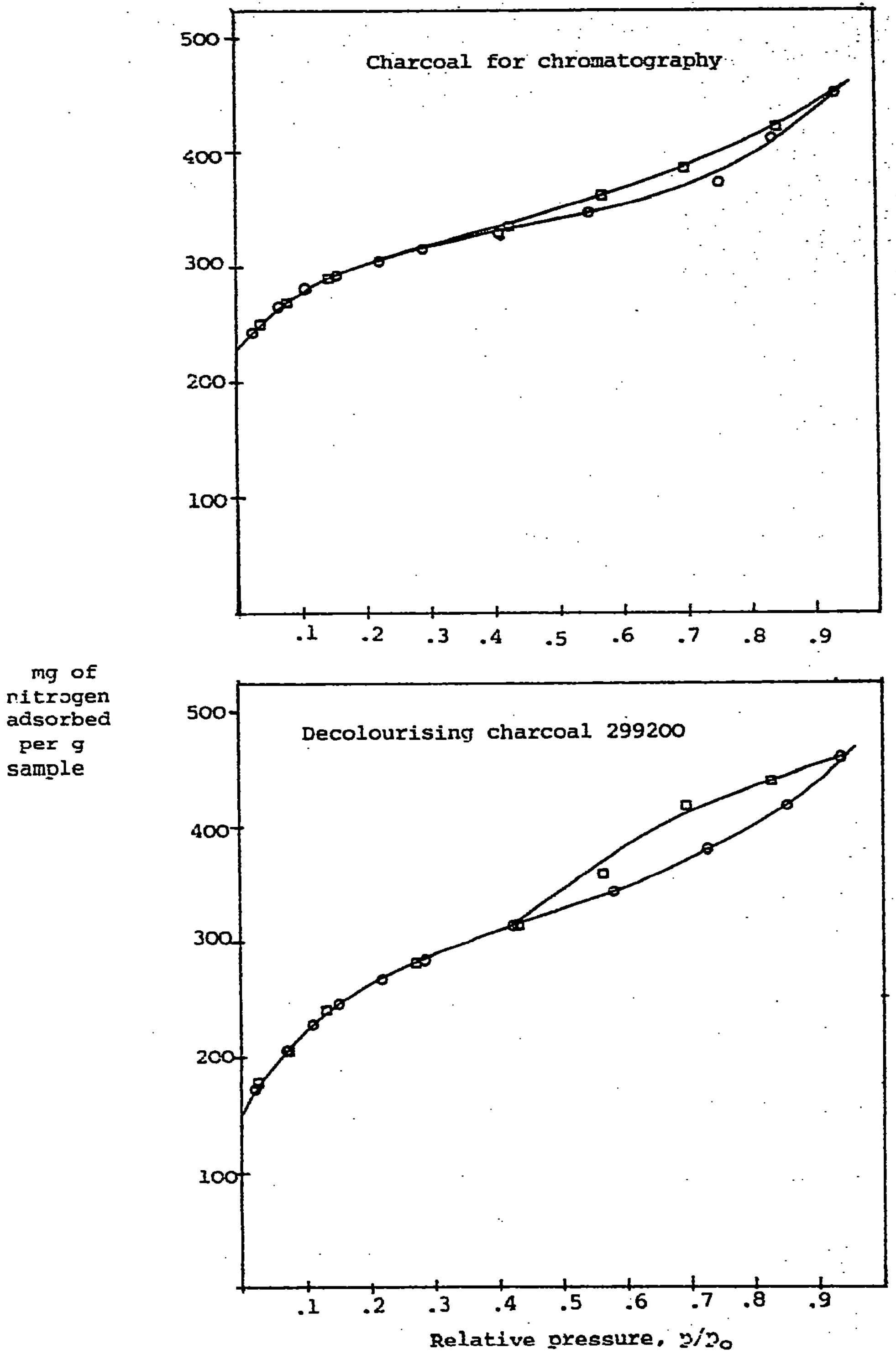

Fig. 3. Adsorption of nitrogen at -196°C on chromatographic and decolourising charcoals

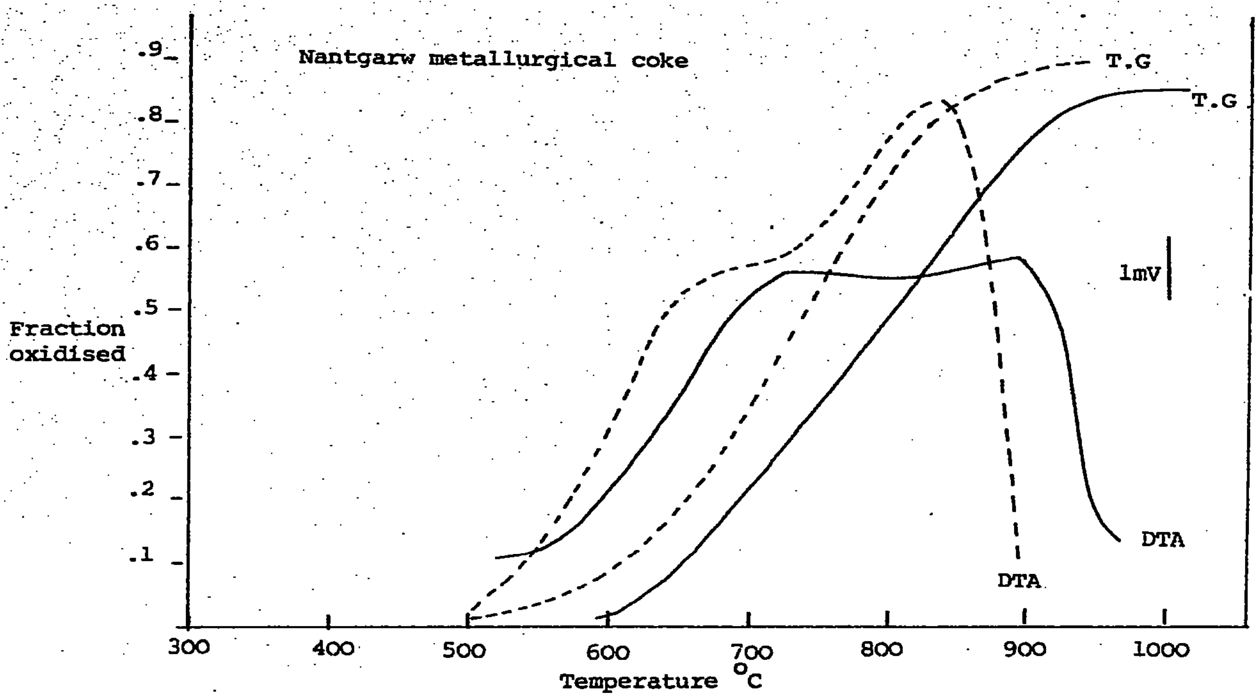

Fig. 4. Oxidation of Nantgarw metallurgical coke (TG and DTA data)

ACKNOWLEDGEMENTS

The authors thank Mr. C.F. Harris, Dr. A.W. Richards and Dr. C. Cross (Imperial Smelting Processes Ltd., Avonmouth, Bristol) for their interest and encouragement in this work, and the Science Research Council and I.S.P. Ltd. for grants for the mass-flow balance and the vacuum microbalance.

REFERENCES

1 C.R. Cross, "Non-ferrous uses of metallurgical coke". Paper delivered to the Midlands Section of the Coke Oven Managers Association and the Institute of Energy. March 1980. I.S.P. Ltd., Avonmouth.
2 D.R. Glasson, J. chem. Soc., 1956, pp. 1506-10.
3 Yang et al., Analytical Chemistry, 48 (12) (1976) 1696-9.
4.Dobovisek et al., Mikrochimica Acta, 4 (1967) 639-50.