SINTERED CARBONS FROM CATALYTICALLY PRODUCED MESOPHASE

M. Braun and K. J. Hüttinger
Institut für Chemische Technik, Universität Karlsruhe, D-76128 Karlsruhe

INTRODUCTION

Sintering of powders from polyaromatic mesophase represents a new route for the production of isotropic structural carbons and graphites with extraordinary mechanical properties [1,2]. In view of the sintering process the mesophase powder represents a high technology product. It is produced by separation of mesophase from mesophase pitch. Spherulitic mesophase was found to be a more useful raw material than bulk mesophase [2]. Therefore, it was attempted to produce a mesophase pitch with an as much as possible high content of spherulitic mesophase. It was achieved by an iron catalyzed mesophase synthesis with soluble iron compounds like ferrocene, iron benzoate or iron naphthoate [4]. The iron, remaining in the mesophase fraction, has a very beneficial side effect. It can prevent sulfur puffing, which otherwise can destroy not only the microstructure but also the complete carbon body. Synthesis of a mesophase pitch from a coal tar pitch with iron benzoate, preparation of the sintering powder and properties of the sintered and graphitization treated carbons will be presented.

EXPERIMENTAL

A filtered coal tar pitch with the following properties was used: THF-IS (tetrahydrofurane insolubles), 17%; NMP-I (N-methylpyrrolydone insolubles), < 1%; S.P. (Mettler), 102°C; CY (coke yield, Alcan), 48,3%; sulfur content, 0,6%. Iron benzoate was synthesized from benzoic acid and $FeCl_3$ [3].
The iron benzoate was mixed with the liquid pitch in such an amount as to give an iron content of 1.5%. The pyrolysis of this mixture was performed at 440°C under an argon pressure of 1MPa using a stirred tank reactor; after 5h reaction time a pitch with a mesophase content of about 50 vol% was obtained. Without iron benzoate the mesophase content only was 15 vol% [4].

Optical micrographs of both pitches are shown in Figs. 1(a) and (b). The catalytically produced pitch was extracted with boiling THF, giving a yield of about 58 %. The resulting powder is too plastic for sintering; it was partially stabilized by oxygen treatment and subsequently milled to a particle size less than 10 μm. The powder was molded by monoaxial pressing at 125 MPa; the bodies were sintered at 1000°C and high temperature treated at 2400°C.

RESULTS AND DISCUSSION

Sintering behaviour of three powders with different thermoplasticity, adjusted by oxygen stabilization, was investigated. Thermoplasticity was determined with a penetration test described elswhere [5]; it is characterized by the percentage of penetration of a conical push rod tip into the sample during heating up. The flexural strength values after sintering at 1000°C in Fig. 2 show that the thermoplasticity of a powder has a tremendous influence, a result which underlines the previous statement that sintering mesophase powder is a high technology material.Treatment of the sintered carbons to higher temperatures has various effects on the strength. It increases in the calcination regime up to about 1400°C, decreases in the puffing regime between 1400 and 1600°C and further decreases in the graphitization regime above 1800°C. A strength increase by calcination is combined with a shrinkage and density increase, the strength decrease in the graphitization regime is caused by recrystallization; after treatment at 2400°C the following crystallographic parameters were determined: c/2 = 0.3374 nm; Lc = 16 nm.
The strength decrease in the puffing regime can neither be caused by sulfur puffing nor by evaporation of iron. Electron probe microanalysis and X-ray diffraction studies showed formation of various iron sulfides already in the mesophase. The release of iron is shown by a dot-dash curve in Fig. 2; it

occurs above 1600°C. In the present state of research nitrogen puffing is believed to be responsible for the strong strength decrease of more than 20 MPa. If any kind of puffing can be prevented, graphitized carbons with a flexural strength of at least 180 MPa can be produced. Mesophases from precursors without heteroatoms are being studied. A most important conclusion can already be drawn from the present results: the maximum achievable strength of a graphitized carbon is predetermined after sintering, in other words by the sintering properties of the mesophase powder.

ACKNOWLEDGEMENT

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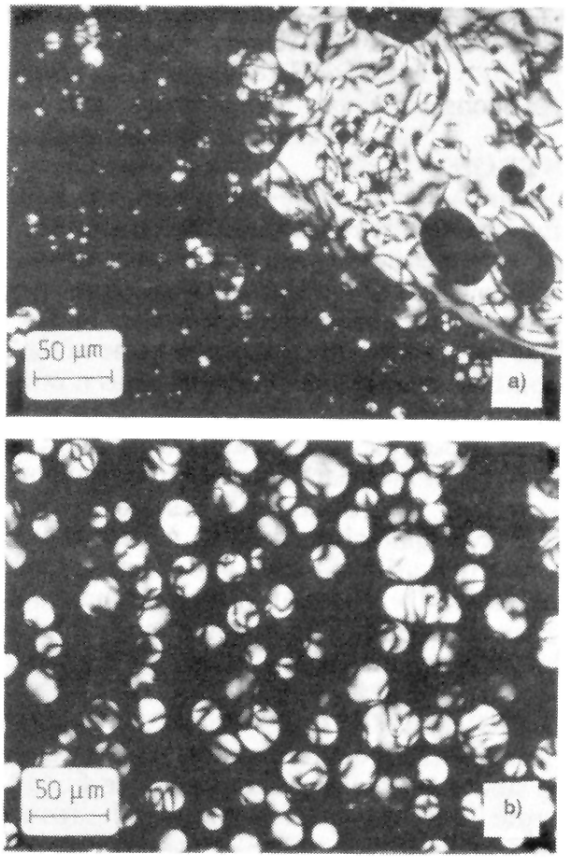

Fig. 1. Optical micrographs of mesophase pitches produced at 440°C and 5h residue time without (a) and with iron benzoate (b).

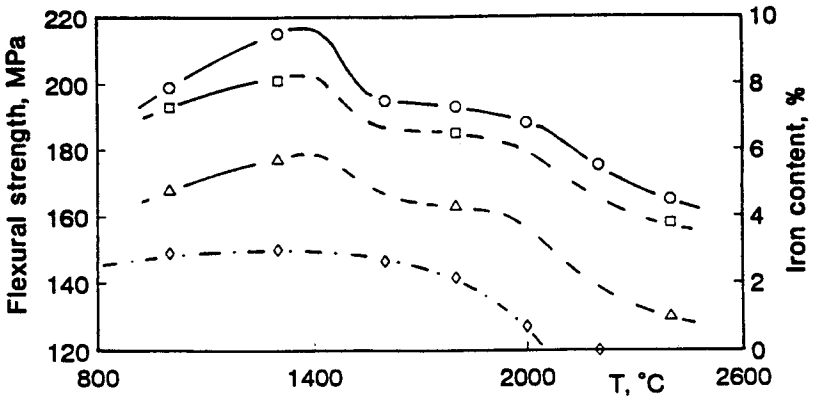

Fig. 2. Flexural strength and iron content in dependence of heat treatment temperature; O, 18%; □, 22%; Δ, 15% penetration; ◊, iron content.