MESOPHASE PITCH AS MATRIX PRECURSOR OF CARBON BONDED MAGNESIA REFRACTORIES

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INTRODUCTION

Carbon bonded magnesia bricks are extensively used as linings of converters and ladles in the steel making industry. Precursors of the carbon matrix are thermoplastic binders such as coal tar pitch and more recently thermosetting binders such as phenol formaldehyde resins, but these are much more expensive. After carbonization, a favourable binder or carbon precursor should give a high coke yield and bricks with low porosity and high cold crushing strength. With coal tar pitch these goals can only be achieved by using carbon (carbon black, graphite) and sulfur additions. For this reason the usefulness of a pure mesophase pitch was studied [1,2]; this was shown in a recent study to be a valuable matrix precursor of carbon fibre reinforced carbon [3].

EXPERIMENTAL

The magnesia used was a typical dead burned dense sinter produced from seawater with a MgO content > 97 %. The grain fractions were selected with respect to a dense packing. Mesophase pitch was produced from the Ashland A 240 petroleum pitch as described elsewhere [2]. The mesophase is absolutely spherulitic, the sphere diameters are in the range from 10 to 25 μm, and the mesophase content amounts to 28 vol.%. Further properties of this pitch and a special coal tar pitch with low BaP content are given in Table 1. The temperature dependencies of the pitch viscosities and magnesia wettability by pitches were studied [1]. At 250 °C, the viscosity of ctp 1 and 2 is two orders of magnitude lower than that of the mesophase pitch. The contact angles are: ctp 1 $\approx$ 5°, ctp 2 $\approx$ 35° and mpp $\approx$ 60°. At 300 °C, the differences are much smaller.

Samples of 30 mm in diameter and 10 mm in height were fabricated by (1) dry mixing of the magnesia grain fractions and pulverized pitch (< 100 μm), and (2) subsequent hot pressing of the mix in an electrically heated die. Some of the samples were stabilized in pure oxygen at a pressure of 1 MPa and temperatures between 160 and 200 °C. All samples were carbonized in an electrically heated laboratory furnace under flowing inert atmosphere. The standard heating rates were 0.2 $Kmin^{-1}$ up to 600 and thereafter 1 $Kmin^{-1}$ up to 1000 °C; residence time at the final temperature was one hour.

RESULTS

Results with samples hot pressed at 250 and 300 °C with pressures of 100, 200 and 300 MPa will be presented in the following. They were characterized by determination of binder and carbon content, bulk density, porosity, intergranular pore volume, coke yield, relative volume change and cold crushing strength (Fig. 1 to 3). Figure 3 also gives the cold crushing strength of samples obtained with the reference pitches.

The effect of the pressing temperature on the properties investigated is very different. At the higher temperature of 300 °C binder and coke yield are lowered, bulk density is increased, and the porosity is nearly unchanged (Fig. 1); the intergranular pore volume and especially the relative volume change of the samples after carbonization are decreased (Fig. 2). Similar influences were found for the pressure. The coke yields are in the range of 75 %. Less than 1 % relative volume change of the sample pressed at 300 °C is very remarkable (Fig. 2).

The values found for the cold crushing strength are more than satisfying; they show a maximum of more than 80 MPa at a pressure used for compaction of 200 MPa. The slight decrease of this value at 300 MPa pressure may not be explained on the basis of the data shown in Figs. 1 and 2, but optical micrograph showed a deterioration of large magnesia grains.

The results presented above have shown that mesophase pitch represents an attractive precursor of the carbon matrix in the production of carbon bonded magnesia refractories. Nevertheless, for drawing a final conclusion reactivity and slag resistance tests have to be and will be performed.

REFERENCES

[1] Vinçon, A. U., Thesis, University of Karlsruhe 1994
[2] Bernhauer, M. et al., Carbon **32** (1994), 1073
[3] Christ, K. and Hüttinger, K. J., Carbon **31** (1993), 731

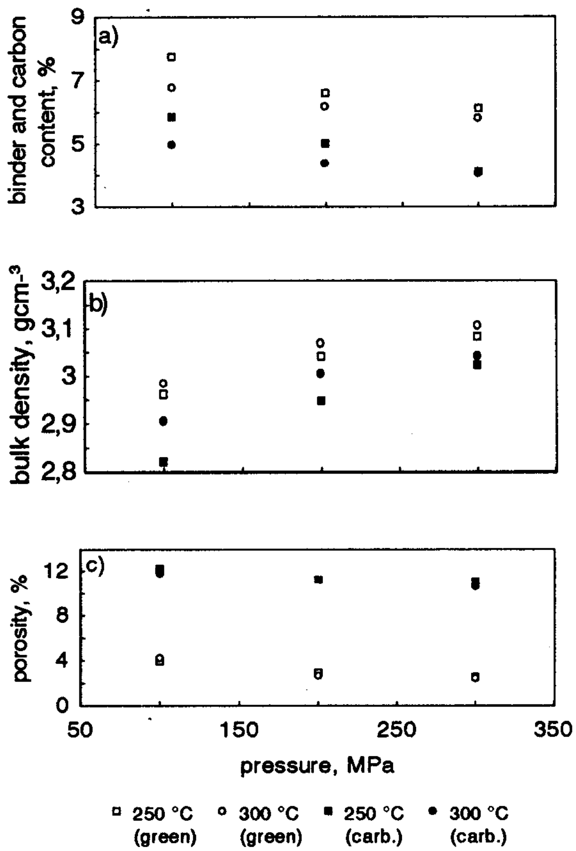

Fig. 1 Measured Properties of the Samples

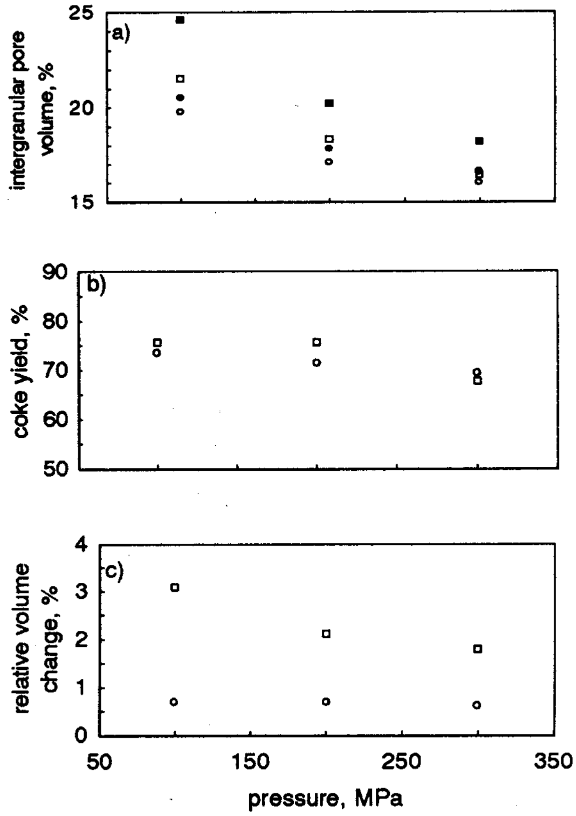

Fig. 2 Calculated Properties of the Samples

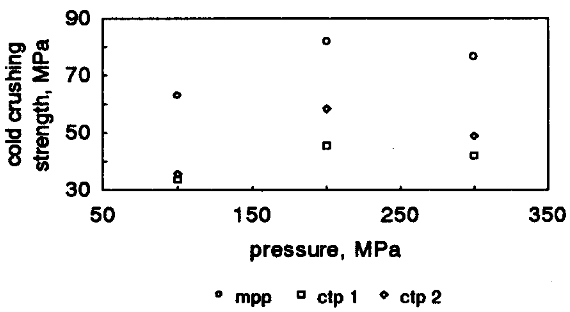

Fig. 3 Cold Crushing Strength

Table 1: Properties of Pitch Binders for Refractory Application

properties	**electrode pitch** (ctp 1)	**ref. special pitch** (ctp 2)	**mesophase pitch** (mpp)
density, gcm^{-3}	1.297	1.295	1.315
THF-IS, %	24.8	37.0	40.4
CY (600 °C)	36.4	53.1	61.0
CY (1,000 °C)	34.7	51.1	58.2
Tg (TMA), °C	≈ 35	54.5	95.8
S. P., °C	68.6	97.0	≈ 155
MC, %	0	0	28
BaP, ppm	≈ 12,000	31	3,750