

An Improved Method for the Rapid, Small-Scale Determination of the Thermal Expansion Coefficient of Needle Coke

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Introduction

In the manufacture of graphite arc electrodes for the steel industry, needle coke is employed as filler to confer a low coefficient of thermal expansion (CTE), and hence good thermal-shock resistance, on the graphite. The measurement of this quantity, which represents one of the primary quality parameters of needle coke for arc-electrode manufacture, is an extremely time-consuming process. The several methods in use in the industry typically mimic the electrode manufacturing procedure: a mixture of milled coke and binder pitch is extruded at a temperature above the softening point of the pitch and the green extrudates are sectioned, baked at temperatures around 850°C, and graphitized at up to 3000°C. The bars may then be machined to produce artefacts of the desired form, which are then employed for the measurement of the CTE, usually by a dilatometric method.¹

There exists a considerable incentive to reduce both the total time required and the manpower involved in making a CTE determination, while for research purposes a method requiring a smaller sample offers advantages. While studying the rheological characteristics of coke/pitch mixtures by means of a capillary rheometer, it was found that the extrudates produced, when processed in an appropriate manner, proved suitable for the determination of the CTE with excellent repeatability and in much less time than required for larger, conventionally produced artefacts.

Experimental

For this study a number of calcined cokes, both commercial and experimental and covering a range of quality, were employed. The experimental cokes were all laboratory-calcined at 1300°C for 6 h (heat-up rate 4 K/min) before CTE measurement.

The extrusion mixes were prepared from milled coke (60% m/m < 75 μ m, 50 g), binder pitch of softening point (ASTM D 36) 92.5°C, crushed to < 1 mm (19.5 g), and Fe₂O₃ (1 g), combined by thorough dry-blending.

For the extrusion a capillary rheometer (Instron or Göttfert Model 2000) with barrel dia. 9.5 mm was employed. (A small extruder operating at constant plunger speed could also be used.) The

nozzle dimensions were: dia. 5 mm, length/dia. ratio 10, entry angle 90°C. Each charge was conditioned in the barrel for 5 min at 125°C and 2.8 MPa pressure before extruding at 125°C and a constant plunger speed of 10 mm/min.

For a given coke/pitch mix, three portions each of 15 g were extruded and from each green rod two 50 mm sections were sawn. The rods were heat-treated, packed in coke granules, in a nitrogen atmosphere at 1300°C for 1 h (heat-up rate 4 K/min, with intermediate dwell of 1 h at 850°C).

Linear CTE's of the six artefacts prepared from each coke sample were measured without further machining of the rods other than grinding to give plane-parallel end-faces, using a six-position quartz push-rod dilatometer. The measurement was made in the contraction mode between an upper temperature of 225°C and, following cooling in the atmosphere, at 25°C.

The procedure for the preparation of 8 mm artefacts from 20 mm extrudates was as given in ref. 2. These were measured using a quartz push-rod dilatometer in the expansion mode between 35 and 235°C. This dilatometer was calibrated using bars of quartz and special glasses 8228 and 8230 (Jena-er Glaswerk Schott & Gen., Mainz, West Germany) having CTE values between $0.6 \times 10^{-6}/\text{K}$ and $2.6 \times 10^{-6}/\text{K}$. The CTE's of these bars were determined by laser interferometry at the Physikalisch-Technische Bundesanstalt, Braunschweig, West Germany.

Results and Discussion

Figure 1 shows the excellent correlation between the CTE's of 5 mm extrudates, prepared as described above and heat-treated at 1300°C, and graphitized 8 mm artefacts machined from 20 mm extrudates. The (provisional) repeatability of determinations made according to the new method is $0.04 \times 10^{-6}/\text{K}$. The principal features of the method are discussed below. Substantial savings in time are realised by the elimination of certain processing steps and by the small scale of the equipment required.

Preparation of the Mix

It was found that simple dry-blending of the components prior to extrusion gave results as good

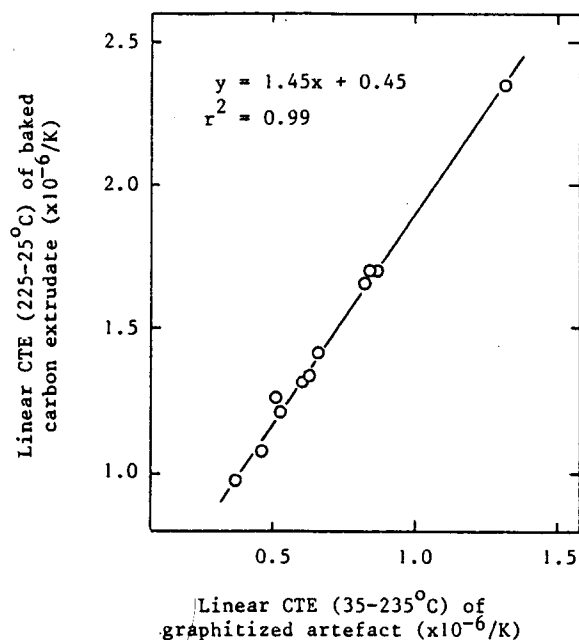


Figure 1. Relationship between linear CTE's of graphitized artefacts (8 mm) and carbon extrudates (5 mm) baked at 1300°C.

as or better than those obtained with blends hot-mixed in a double-sigma-bladed mixer. This is probably because the number of variables that may not be exactly reproduced each time is greater in the case of hot-mixing. Also, even with an unvarying mixing procedure, the degree of shear applied to the mix will depend on its viscosity, which may vary from coke to coke.

Extrusion

The reduction ratio (barrel dia. to nozzle dia.) of about 2 is the minimum required to give extrudates having a sufficient degree of orientation of the filler particles, as shown by Wagner et al.³ It was found that mixes extruding at pressures below about 7 MPa tended to give poor results, which could be improved by increasing the plunger speed.

Heat Treatment

By measuring the artefacts in the baked state the graphitization step could be eliminated. Correlations between the CTE's of baked and graphitized artefacts have been described by Wagner et al. and by Kakuta et al.^{4,5} For the small rods and short baking cycles of the present method the conventional baking temperature of 850°C was found to give insufficiently reproducible results and a

heat-treatment temperature of 1300°C was adopted, as described elsewhere.²

CTE measurement

The baked rods received no further treatment other than end-grinding to give plane-parallel faces, in contrast to methods which involve machining the entire extrudate in order to eliminate surface effects. Measurement of the rods in contraction mode (temperature first high, then low) means that thermally preconditioning the rods, as was found necessary when measuring in expansion mode, is not required.

Conclusion

While for specification purposes the CTE measured on graphitized artefacts may continue to be required, the accelerated method described above is of value for forming rapid estimates of the CTE for process-control purposes. The scale - smaller by an order of magnitude, in terms of coke intake, than other commonly used methods - makes it attractive for the evaluation of small quantities of coke produced in laboratory-scale cokers.

References

1. For examples of published methods of artefact preparation and CTE measurement, see proposed specification AKK 22, "Herstellung von strang-gepressten Probekörpern aus calcinierten Koks," Arbeitskreis Kohlenstoff der Deutschen Keramischen Gesellschaft, October 1981, and specification DIN 51 909, "Bestimmung des linearen thermischen Ausdehnungskoeffizienten: Feststoffe," Deutsches Institut für Normung, February 1984.
2. R.S. Downing and D.A. Borger, "Thermal Expansion Coefficients of Baked and Graphitized Carbon Extrudates," Extended Abstracts, 17th Biennial Conference on Carbon, Lexington, Ky., U.S.A., June 1985.
3. M.H. Wagner and G. Wilhelmi, "Influence of Reduction Ratio and Extrusion Rate on Anisotropy of Graphite Artefacts," Extended Abstracts, 6th London International Carbon and Graphite Conference, London, England, September 1982, 13-15.
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5. M. Kakuta et al, "Relationships between Properties of Calcined Cokes and Characteristics of Graphitized Rods Derived from them," Extended Abstracts, International Symposium on Carbon, Toyohashi, Japan, 1982, 61-64.