Thermal Expansion Coefficients of Baked and Graphitized Carbon Extrudates

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Introduction

Graphite electrodes for application in the electric-arc furnace steelmaking process are manufactured by extruding mixtures of coke and binder pitch. The green blanks are baked at temperatures around 850°C to convert the pitch to binder coke, before being graphitized at up to 3000°C.[1,2]

An important characteristic of needle coke for electrode manufacture is a low coefficient of thermal expansion (CTE), which is necessary to give electrodes having sufficient resistance to thermal shock. In the evaluation of coke for this application the CTE is measured on small coke/pitch extrudates, which are baked and graphitized in a similar way to that applied to commercial electrodes. This is a time-consuming procedure and there is considerable interest in shortening it. One way to do this is to measure the CTE on the baked artefacts,[3,4] thereby eliminating the graphitization step.

During the development of a rapid, small-scale method of CTE measurement,[5] studies on the relationship between the CTE's of baked and graphitized artefacts showed that the correlation obtained is strongly dependent on the temperature programme applied during the baking cycle. The results obtained provide information relating to the change of properties of coke/pitch artefacts during baking.

Experimental

The cokes studied in this investigation ranged in quality from regular-grade to needle cokes and had sulphur contents between 0.3 and 1.7% m/m. Both commercially calcined and experimental cokes were studied, the latter following laboratory calcination at 1300°C for 6 h (heat-up rate 4 K/min). Two types of artefact were prepared for CTE measurement.

To prepare artefacts from 20 mm extrudates, coke flour (60% m/m <75 μm, 500 g) and binder pitch of softening point (ASTM D 36) 92.5°C (167 g) were combined at 110°C in a double-sigma-bladed mixer with Fe_2O_3 (10 g) and extrusion oil (5 g). Rods of 20 mm dia. were extruded at 125°C using an oil-pressure ram extruder. The green rods were sectioned and baked, packed in coke granules, in a nitrogen atmosphere at 850°C for 3 h (average heat-up rate 0.75 K/min), following which some were graphitized at 3000°C. For CTE measurement, 50 mm cores of 8 mm dia. were bored from the 20 mm extrudates.

For the preparation of 5 mm extrudates, coke flour (60% m/m <75 μm, 50 g), binder pitch crushed to <1 mm (19.5 g) and Fe_2O_3 (1 g) were combined by thorough dry-blending. Green rods of 5 mm dia. were extruded from a capillary rheometer (Instron) at a constant plunger speed of 10 mm/min, following conditioning in the rheometer barrel for 5 min at 125°C under a pressure of 2.8 MPa. The green extrudates were sectioned and baked for 1 h at temperatures between 850 and 1300°C (heat-up rate 4 K/min). For temperatures higher than 850°C an intermediate dwell of 1 h at 850°C was given. Some of the baked rods were graphitized at 3000°C.

The linear CTE's of both the 8 mm artefacts and the 5 mm extrudates were determined using quartz push-rod dilatometers.

Results and Discussion

Figure 1 shows the correlation between the CTE's of (850°C) baked and graphitized 8 mm artefacts machined from 20 mm extrudates. Similar relationships have been demonstrated by Kakuta et al and by Wagner et al.[3,4] The baked-artefact CTE is always higher than the graphitized value, suggesting that the structural features responsible for accommodating thermal expansion internally are only incompletely developed in baked bodies.

In contrast to the results obtained with the 8 mm artefacts, the CTE's of the 5 mm extrudates, baked at 850°C, showed scarcely any correlation with the graphitized values. Better results were obtained when the extrudates were baked at higher temperatures and it was found that heat treatment at 1300°C gave an excellent correlation, suitable for use in predicting the graphitized value, as shown in Figure 2.

The use of 850°C as the baking temperature for rods intended for CTE measurement stems from the fact that this is the temperature employed for baking electrode blanks prior to graphitization. However, much research on the calcination of petroleum coke has shown that many coke properties

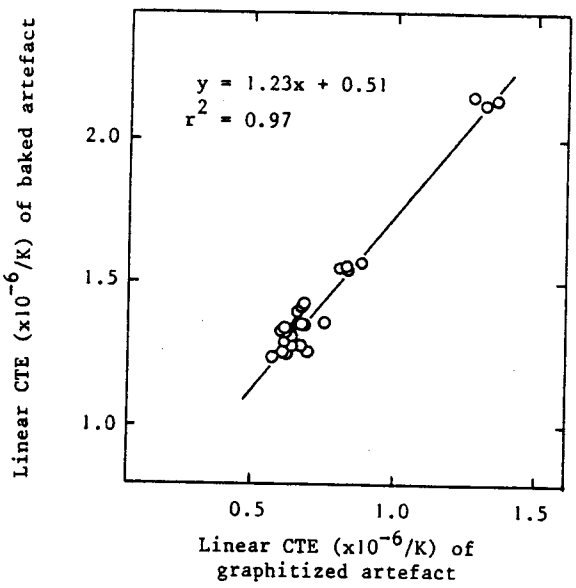

Figure 1. Relationship between linear CTE's (35-235°C) of baked (850°C) and graphitized 8 mm carbon artefacts from 20 mm extrudates.

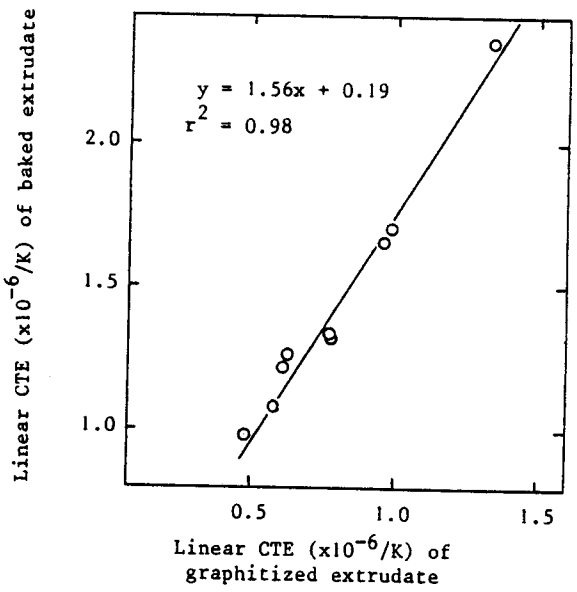

Figure 2. Relationship between linear CTE's (225-25°C) of baked (1300°C) and graphitized 5 mm carbon extrudates.

are undergoing rapid change in the region 600-900°C.[6] Investigations into the heat treatment of binder coke and electrode blanks suggest that the same is true for these materials also.[7,8] With a baking temperature of 850°C stabilization may be achieved by the use of very long baking cycles but this is not desirable in a procedure for rapid CTE measurement.

A baked body is a composite of filler and binder cokes. It is the filler-coke that primarily determines the CTE of the artefact.[3] Since this component has already been exposed to temperatures equal to or greater than 1300°C during calcination it is unlikely that its contribution to the CTE of the composite will be altered by raising the baking temperature. It is suggested that some feature of the composite, involving perhaps the filler/binder interface, makes a variable and unreproducible contribution to the total CTE in the case of insufficiently baked artefacts. When a degree of annealing sufficient to stabilize the composite is given by a suitable temperature/time profile the CTE, measured on the baked artefact, is free of extraneous influences and accurately reflects the graphitized value.

References

1. E.L. Piper, "Processing of Baked and Graphitized Carbon," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 4, John Wiley and Sons, New York, etc., 1978, pp. 576-88.

2. O. Vohler et al, "Kohlenstoff," Ullmanns Encyklopädie der technischen Chemie, 4e Auflage, Band 14, Verlag Chemie, Weinheim and New York, 1977, pp. 595-691.

3. 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.

4. M.H. Wagner et al, "Aspects of Thermal Expansion of Baked and Graphitized Carbon Artefacts," Extended Abstracts, International Carbon Conference 'Carbone 84,' Bordeaux, France, July 1984, 410-11.

5. R.S. Downing and D.A. Borger, "An Improved Method for the Rapid, Small-Scale Determination of the Thermal Expansion of Needle Coke," Extended Abstracts, 17th Biennial Conference on Carbon, Lexington, Ky., U.S.A., June 1985.

6. P. Rhedey, Trans. Metallurgical Soc. A.I.M.E., 1967, 239, 1084-91.

7. J. Bogucki et al, "The Influence of Baking Conditions on the Properties of Green Electrodes," Extended Abstracts, 15th Biennial Conference on Carbon, Philadelphia, Pa., U.S.A., June 1981, 339-40.

8. J.S. Evangelides and G.S, Rellick, "Properties of Cokes from Binder Pitches as Functions of Processing Temperature and Pressure," Extended Abstracts, 14th Biennial Conference on Carbon, University Park, Pa., U.S.A., June 1979, 405-6.