

THERMAL EXPANSION OF MICROCONSTITUENTS OF COKE

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Introduction

Polycrystalline graphites for electric-arc-furnace electrodes and aerospace applications should have low coefficients of thermal expansion to be thermally shock-resistant. The type of filler coke directly influences the thermal expansion of bulk graphite; measurements of the thermal expansion of graphites fabricated from a variety of cokes have shown the dependence of thermal expansion on the filler coke [1]. The low volumetric thermal expansion of polycrystalline graphites and cokes, in all cases lower than the volumetric thermal expansion of single crystal graphite, has been attributed to the degree of preferred orientation of the crystallites [2] and to accommodation of the crystallite c-axis expansion by intercrystalline voids [3]. The preferred orientation depends on the structure of the filler coke particles and on the fabrication process. It has become apparent that accommodation appears to relate to the development of shrinkage cracks upon the initial heat treatment of semi-cokes [4].

As a class, graphites fabricated with needle cokes have the lowest coefficients of thermal expansion. Previous work on the thermal expansion of needle cokes [4, 5] has shown that the fine fibrous microconstituent, which constitutes only a portion of a typical delayed needle coke [6], is anisotropic in its thermal expansion. The fine fibrous structure, consisting of folded, corrugated arrays of graphitic layers that are straight and parallel along the needle axis, has a low thermal expansion parallel to this axis that is a function only of the crystallite a-axis expansion. In the transverse direction, the thermal expansion is slightly higher, but less than the thermal expansion of the complex, three-dimensional morphology of a fine isotropic coke. It was also shown that the thermal expansion in the transverse direction of green needle coke had a very high thermal expansion and that the thermal expansion was reduced significantly with heat treatment to only 700-800°C [4, 7].

Understanding the mechanism of accommodation of thermal expansion of an individual coke microconstituent involves relating the coke morphology and microcrack structure to heat-treatment temperature and the intrinsic thermal expansion of the coke itself. Thus, the objectives of this work were to measure the thermal expansion of the fine fibrous microconstituent of needle coke and the fine isotropic microconstituent of an isotropic coke as a function of heat treatment temperature and to observe the changes in microstructure with heat treatment.

Experimental

Thermal expansion specimens 4mm square by 10mm long were cut from larger pieces of Marathon and Carborundum premium needle cokes that had a distinctive needle shape and appearance. The long dimension was normal to the needle axis. Specimens of a fine isotropic (Robinson) coke and an isotropic coke prepared from an Edginton asphalt pyrolyzed to 425°C were also prepared. The ther-

mal expansion was measured with a Leitz quartz dilatometer to 400°C after each heat treatment. In some cases, the same specimens were successively heat treated to higher temperatures and measured.

Results

The effect of heat treatment on the thermal expansion in the transverse direction of the fine fibrous microconstituent and on the thermal expansion of the fine isotropic microconstituent is shown in Fig. 1, along with similar measurements by Mochida [5]. For both microconstituents, a significant reduction in thermal expansion occurred upon heat treatment to only 700°C. This reduction in expansion is related to the development of shrinkage cracks associated with the densification of the green coke. The real density of green coke increases from 1.4 g/cc near 600°C to about 2.2 g/cc at 1400°C [8], producing these shrinkage cracks. Little reduction in thermal expansion occurred upon heat treatment to graphitizing temperatures.

Micrographic evidence of the formation of shrinkage cracks upon heat treatment of the green cokes is given in Figs. 2 and 3. For the fine fibrous microconstituent, a significant increase in the number of shrinkage cracks occurred between 550 and 600°C. On heating to 1100°C, the shrinkage cracks widened, but did not noticeably increase in number. At 600°C, shrinkage cracks also occurred in the fine isotropic microconstituent (Fig. 3), whereas they were not present at 425°C. The shrinkage cracks in the fine fibrous microconstituent tend to be large compared to its folded, corrugated morphology as characterized by polarized-light extinction contour spacings of 1 to 10 microns. The cracks which run parallel to the layers along the needle axis, can extend fairly easily in the transverse direction. In contrast, the shrinkage cracks in the isotropic microconstituent are quite small as the cracks are confined by the doubly-curved layers of its complex, three-dimensional morphology.

The thermal expansion of green mesophase coke is higher than that for crystalline graphite. This may be explained by the fact that at this stage extensive polymerization has not begun and the individual molecules are bonded by van der Waals forces both perpendicular and parallel to the plane of the molecule. The low density of green coke implies that the free volume of a typical mesophase molecule is 60% greater than a region of a graphitic basal plane with a similar mass. This free volume would allow greater thermal motion and thus a high thermal expansion in both directions.

This work has shown that the two coke microconstituents, fine fibrous and fine isotropic, which result from different precursors [8], have different thermal expansions and that for both the shrinkage cracks introduced by heat treatment to only 700°C act as accommodation sites. However, within a typical needle coke produced from a deformable mesophase precursor, there are several distinct

microconstituents of which the fine fibrous structure is just one. Relating the thermal expansion of these other microconstituents to their morphology and shrinkage crack structure may thus lead to the identification of a coke morphology, and a coking process, that would have an even lower thermal expansion than the fine fibrous microconstituent.

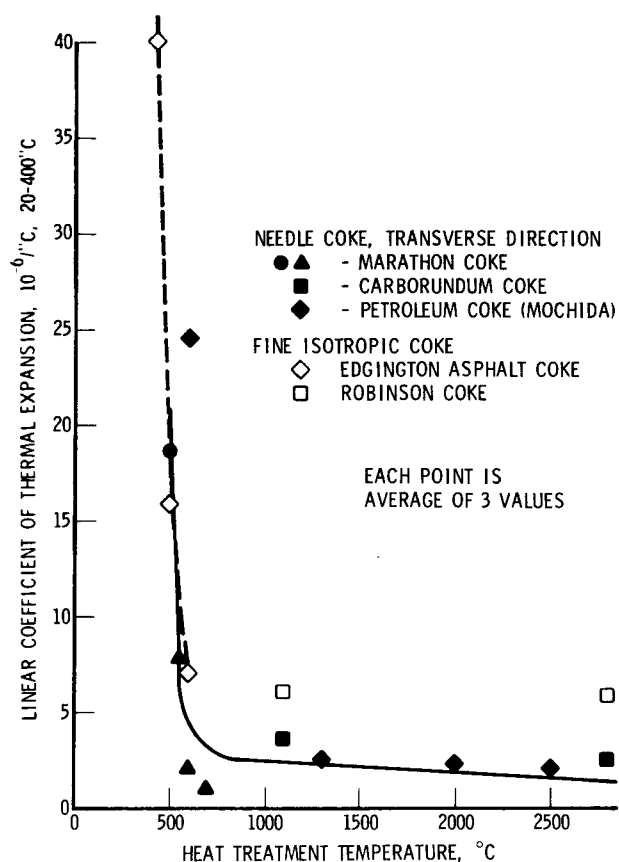


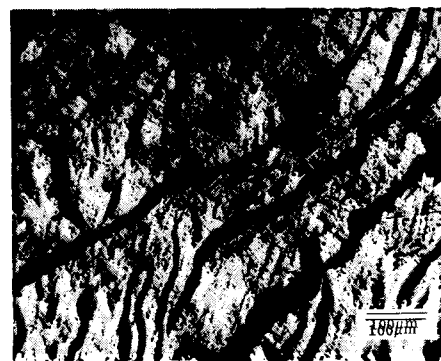
Fig. 1. Effect of heat treatment on thermal expansion of fine fibrous and isotropic microconstituents. The data by Mochida [5] are for temperature range of 350-450°C.



550 C



600 C



1100 C

Fig. 2. Shrinkage cracks in transverse cross section of fine fibrous microconstituent, polarized light.

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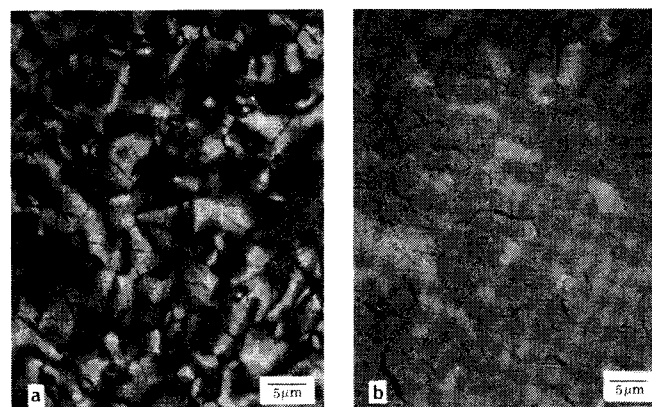


Fig. 3. Shrinkage cracks in fine isotropic microconstituent heat treated to 600°C; (a) cross polarizers, (b) bright field.