

Puffing in Cokes: A Possible Mechanism

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Abstract. The phenomenon of puffing is related to rates of graphitization, the nature of the gas evolved, porosity and structure within the coke. Evolution of gases containing sulphur and nitrogen appear to be the cause of the problem. Cokes of low CTE with large-sized optical texture are most susceptible to puffing. Additives can reduce extents of puffing. Analyses of high resolution lattice image electron micrographs in terms of the detail of atom movement suggest the cause of puffing. Rigid convoluted structures are formed 1200-1700 K in needle-cokes.

Introduction

The phenomenon of puffing. The irreversible volume expansion on heating of coal-tar pitch cokes and petroleum cokes around 1600°C is known as "puffing". Because it is associated with a decrease in coke density and coke strength it is a phenomenon detrimental to coke quality for electrode manufacture. The cause of puffing is linked to sulphur and nitrogen contents of the cokes, a build-up of gaseous products evolved during the heat treatment within 'closed porosity' eventually being explosively released causing damage to the coke structure.

It is thought that differences in the volume distribution of sulphur within coke are too small to create these pressure differentials. Similarly, differences in behaviour between sulphur bound to carbon and to oxygen do not correlate closely with sulphur content but the correlation can improve if the puffing behaviour is linked to the total of sulphur and nitrogen contents. During heat treatment of cokes, sulphur removal appears to accelerate in the temperature ranges 1400-1600°C and 1800-2000°C. Nitrogen removal occurs in the range 1200°C-1600°C and is virtually complete at 1600°C.

It would appear that non-graphitizable carbons are less susceptible to puffing than graphitizable carbons (1). References which discuss puffing stress the role of coke structure, but find it difficult to use specific models. It is suggested by Sugimoto *et al.* (2) that heteroatom removal causes disruption of the relative alignment of neighbouring crystallites. Puffing can be reduced by keeping the temperature between 1400-1600°C for a few hours during graphitization (Fujimoto *et al.*) *i.e.* by slowing-down rates of gas evolution. Conversely, rapid heating of the carbon artefact increases the extent of damage by puffing. Letizia and Wagner (3) emphasize that puffing is due to a structural change in the coke. An important observation is that for a range of cokes, as the CTE value decreases, so puffing increases despite the fact that cokes of low CTE have a porosity adequate to accommodate the thermal

expansion of the coke. It is suggested that the main difference between cokes of low and high CTE (high and low puffing characteristics) is associated with the larger size of constituent molecular lamellae within cokes of low CTE (Fujimoto *et al.*). The expression is introduced into the literature that at about 1800°C the carbon body softens (4). Heintz (5), in a study of crystallite growth and ordering in the pre-graphitizable range reports that puffing temporarily disrupts crystallite growth before the final stage of graphitization is initiated at temperatures in excess of 2100°C. An observed decrease in the helium density during puffing is an indication of a significant increase in closed pore volumes of the expanded crystallites, so introducing imperfections. Fitzer *et al.* (6) using dilatometric in situ measurements during heating of petroleum cokes, recorded pore volume and pore size distribution data.

Puffing behaviour can be inhibited or at least moderated by the addition of inorganic compounds of high chemical affinity for sulphur. Fitzer *et al.* (7) found the inhibition effect was almost independent of the grain size of the coke. The irreversible puffing is caused mainly by sulphur in fine-grained particles such as the flour of the carbon mixes. These authors (8) discuss the affinity between inhibitors and sulphur, including their melting behaviour, and that of intermediates. The diffusion to grain boundaries of sulphur appears to be the rate controlling step.

The immediate problem in explaining the phenomena of puffing is to relate this behaviour to the detail of alignment and structure of the constituent 'lamellae' of the coke within the crystallite to the porosity of the coke. Although the method of X-ray diffraction clearly identifies the phenomena of puffing (5), this method is not sufficiently refined to provide information at the level of the constituent lamellar plane. The only technique available for this is high resolution, phase contrast transmission electron microscopy (HREM) which, via an inter-

ference procedure, can provide fringe images which are related to the size, shape and stacking arrangements of the constituent lamellar planes. The objective of this paper is to consider the information which is available from published studies of HREM and to assess if an explanation(s) of puffing can be developed therefrom. The use of scanning electron microscopy of a grist coke particle could also be informative.

High resolution electron microscopy (HREM). Crawford and Marsh (9) indicate how HREM may be used to study structure in carbons. Millward and Jefferson (10) review the available literature to 1978. Marsh and Crawford describe structural changes on heating a coal-tar pitch 477-875°C (11) with Marsh and Griffiths (12) illustrating changes in structure on heating pitch cokes 827-1727°C. Auguie et al. (13) likewise show lattice fringes in pitch coke HTT <2000°C.

Discussion of puffing. Figure 1 is a SEM micrograph of a surface of a grist coke particle and illustrates aspects of puffing referred to in the Introduction. Position A is a section of quite uniform structure, ~50 µm across, with the basal plane structure parallel to the surface of the micrograph. It is free of microporosity. Position B is a macropore ~20 µm diameter with Position C showing a stacked or almost sedimentary nature to structure of the pore wall (14), again without obvious porosity. The needle-like component, transverse cross-section Position D, exhibits porosity 1-2 µm dia. Should gaseous products be created within the bulk of the carbon, then the problem of egress of these gases is apparent.

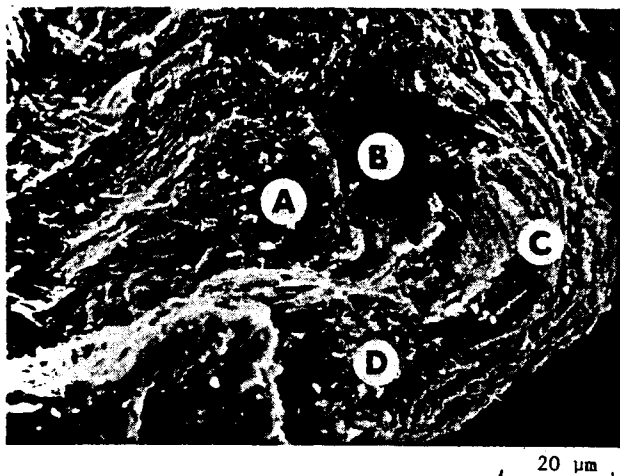


Figure 1. SEM micrograph of a surface of grist coke.

Figure 2 is a model structure (12) based on many lattice imaging micrographs, of the changes on heating mesophase HTT <827°C (1100 K) to graphite HTT >1727°C (2000 K). The central portion represents structure HTT 1227-1723°C (1500-2000 K) depicting a convoluted arrangement of lamellae within the carbon. This convoluted structure could restrict both separation of the lamellae and also the displacement laterally of the lamellae. It is within these arrangements of lamellae that gaseous products are generated stretching over distances of tens of micrometers without grain boundaries, as in Figure 1. With increasing HTT, gaseous products are generated,

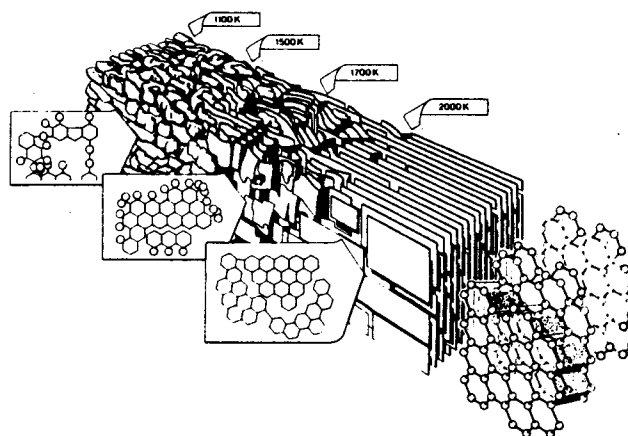


Figure 2. Model structure based on micrographs.

pressures are built-up and the transformation from the convoluted to the parallel (graphitic) structure occurs. The locking-in effect of the convoluted structure maintains pressures for a while until released either by explosive expansion sideways of lamellae or by displacement of the parallel (unpinned) structures; i.e. the formation of plastic or soft carbon which develops with increasing HTT (4). The closed porosity can be created by this mechanism (5).

For the cokes of high CTE with smaller sized optical textures, two factors mitigate against puffing. Diffusion of gases could occur from a greater area of coke surface at the interfaces between the textural units. Also, there does not appear to be a mechanism for formation of convoluted structure. The carbons of small sized optical texture show lattice images of smaller, irregularly shaped and stacked lamellae (15).

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