THE REACTIVITY TO ATOMIC OXYGEN AND CARBON DIOXIDE OF ANISOTROPIC CARBONS OF DIFFERENT OPTICAL TEXTURE

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Introduction

The Northern Carbon Research Laboratories study aspects of the formation of graphite electrode material and metallurgical coke. If the electrode is to be used in steel manufacture, then like metallurgical coke, it is subject to extreme operating conditions of mechanical stress, of high temperature and of oxidation (gasification). The consequence of mechanical and thermal stress and of gasification is the development of fizzures, the propagation of which results in breakage of the graphite and coke and a serious diminution in operating performance. The origins and extent of development of deformation, shrinkage and gasification fizzures, therefore, are aspects of considerable practical importance and warrant investigation at the fundamental level.

Optical Texture

Polycrystalline, synthetic graphites and cokes are structurally heterogeneous materials with considerable porosity, some mesoporosity but mainly macroporosity. The structural heterogeneity is beautifully revealed by examination of polished sections in reflected polarized light using a half wave retarder-plate between the specimen and the analyzer to produce a range of interference colours (i.e. the optical texture). Isochromatic areas can be seen varying in size from <1.0 μm to >200 μm. These isochromatic areas owe their origin to the growth of nematic liquid crystals and mesophase from the fluid phase of the carbonization system (Ref. 1, 2).

An essential aspect of the formation of isochromatic areas of various sizes is the viscosity of the mesophase and its temperature dependence. A relatively low viscosity and an associated relatively long temperature zone of low viscosity permit the growth units of mesophase (when large enough to make contact), to coalesce together so that the identity of the original growth units is lost. This coalescence process is a complicated entwining of the flow-sheets of stacked lamellae (the mesophase), this process eventually establishing isochromatic areas of size, larger than the growth units as well as the various forms of 'disclination' as described by White (Ref. 3, 4). These disclinations are essentially zones of extensive deformation of stacked lamellae. A relatively high viscosity and a short temperature zone of high viscosity, apparently, do not permit the coalescence of the growth units (of smaller size). On making contact, these growth units fuse or adhere together and their identity is not lost. The resultant pattern of small, fused, isochromatic areas appears, under the optical microscope, as a mozaic. This is the characteristic feature of many metallurgical cokes.

Fizzuring and Optical Texture

A research theme of The Laboratories is an appraisal of the origins of mechanical, thermal and gasification fizzures in terms of the optical texture of the carbons. It is established that shrinkage cracks in the large isochromatic areas of carbons from selected grades of coal-tar and petroleum pitch are associated with cleavage parallel to basal planes, within the isochromatic areas, and also at positions of extensive deformation, i.e. the disclination (Ref. 3, 4). The situation with regard to optical textures of diminishing size is less clear, except for the knowledge that in metallurgical cokes the regions composed of small mozaics are not susceptible to cleavage. This raises the question as to the nature of the attachment between the small isochromatic mozaics.

The Experimental Approach

A programme of work was therefore initiated to prepare carbons, from known source materials, having different optical textures ranging from the large isochromatic areas of the needle-cokes to the fine mozaics in carbons prepared in the laboratory from Gilsonite pitch. Part of the programme was heat-treatment to temperatures >2300 K and the examination of carbons by optical and scanning electron microscopy. Polished surfaces can be prepared of low temperature carbons (HTT <1200 K) and the same area re-examined after progressive heating to the highest temperatures.

Another approach is to react the low temperature carbons with atomic oxygen at about 300 K and with carbon dioxide at about 1100 K. Atomic oxygen is known to react preferentially at defects in the graphite lattice (Ref. 5); it was therefore postulated that a similar reaction may occur with anisotropic carbons. Accordingly, carbons were prepared based upon A200 Ashland petroleum pitch, D112 coal extract (National Coal Board) and Gilsonite pitch. These carbons exhibited a range of optical texture. The atomic oxygen was generated using a "Microtron 200" micro-wave generator with an air-cooled resonant cavity, at an oxygen pressure of about 0.1 kPa. Reaction times were 3 minutes. Atomic hydrogen was also used for periods of about 15 minutes.

Discussion

It was found for carbons based on A200 Ashland petroleum pitch that both the atomic hydrogen and oxygen reacted preferentially with parts of polished surfaces to produce channels about 5 μm diameter. Using the colours of the optical texture, reaction occurred at positions of disclinations and within the isochromatic areas. The major part of the polished surface was hardly affected. No such preferential channelling was found using carbons of small mozaic texture. There was some non-uniform gasification of the surface, the non-uniformity being of the same size (SEM) as seen in optical microscopy (2 μm). The appearance resembled that of surfaces of cokes subject to argon-ion bombardment (Ref. 6).

Gasification by carbon dioxide of these carbons also produced quite different effects. With carbons of large isochromatic domains, deep gasification fizzures were a common feature; no comparable fizzures were produced in carbons with an optical texture of small mozaics, only a roughening of the surface resulted.

It is possible that selective etching by the atomic gases occurs at positions of extreme deformation or stress where micro-fizzures may already be in existence, but in size are beyond the limits of resolution of the optical microscope. Gasification by carbon dioxide may follow a similar mechanism. Etching by atomic gases may provide a useful method of assessing the shrinkage characteristics (in low HTT carbons) of graphitizable carbons. The processes of selective, structural etching by carbon dioxide remain intriguing.

References

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